

Concentration Susceptibility and the Phase Diagram
of He^3 - He^4 Mixtures near the Tricritical Line

A Dissertation presented

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STATE UNIVERSITY OF NEW YORK
AT STONY BROOK

THE GRADUATE SCHOOL

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Abstract of the Dissertation

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The variation of He³ concentration with height is measured in the lower phase of He³ - He⁴ mixtures near the tricritical point (TCP), at pressures of 2.5, 9.9, and 16.7 atmospheres. A moveable plunger is used to vary the height of the phase boundary relative to a tunnel diode oscillator concentration sensor. The sample is isolated at low temperature to maintain concentration integrity. Relative shifts of 0.0002 in concentration and 0.06 mm. in height are discernable.

The variation is shown to fit a functional form of $Ax^6 = Z$ where x is the relative change in concentration from its critical value and Z is the vertical distance below the interface. When x is expressed in mole% and Z in centimeters, the parameters take on the values given below at the pressure investigated.

<u>Pressure(atm.)</u>	<u>$A \frac{\text{cm.}}{(\text{mole}\%)^2}$</u>	<u>δ</u>
2.5 ± 0.1	4.7 ± 0.9	1.94 ± 0.2
9.9 ± 0.1	7.3 ± 5	1.81 ± 0.48
16.7 ± 0.1	6.8 ± 2	2.10 ± 0.2

The thermodynamics of He^3 - He^4 mixtures and the scaling hypothesis are discussed. The relationship between the gravitationally induced concentration gradient and the concentration susceptibility, $(\partial X / \partial \Delta)_{\text{TP}}$, is derived. It is shown that δ is the critical exponent defined by $(X - X_c)^\delta = (\Delta - \Delta_c)$. Values of $(\partial X / \partial \Delta)_{\text{TP}}$ are calculated from the data and compared with values measured at saturated vapor pressure by other researchers.

The theoretical models of van Leeuwen and Cohen, Blume, Emery and Griffiths and Takagi are discussed. The values they predict for δ are presented. An attempt is made to understand the pressure dependence of the concentration susceptibility in the light of these models. Improved determinations of the scaling properties of these models near the TCP are briefly discussed.

Values of the concentration gradient are used to provide gravitational corrections to data of Johnson and Rohde. Corrected data showing the motion of the TCP between saturated vapor pressure and 22 atm (the tricritical line) are presented. The determination in this work that the tricritical concentration

takes on its maximum value at 9.9 ± 0.4 atm is incorporated in this presentation. Comparisons are made between the pressure dependence of: the $T=0$ K solubility of He^3 in He^4 , the value of X_c , and the magnitude of the concentration susceptibility.

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I. Introduction

Isotopic mixtures of He^3 and He^4 display some very unusual behavior in the liquid phase. The experimentally accessible thermodynamic variables for the investigation of this behavior are: the temperature $-T$; the pressure $-P$; and the molar concentration of He^3 $-X$. Upon cooling, provided that $X \leq 0.67$, the entire mixture will become superfluid at some temperature, T_λ . This higher-order, superfluid phase transition is known as the "lambda" transition because of the characteristic shape of the associated specific heat curves. T_λ is a monotonically decreasing function of X which maps out a line in $T-X$ space known as the "lambda line".

Upon further cooling, provided that $X \geq 0.10$, the mixture undergoes a first-order phase transition, separating into two liquid phases of different X . The upper phase, rich in He^3 floats on the denser, He^4 -rich phase. The He^4 -rich phase is superfluid. This phase transition can also be displayed in $T-X$ space as a "coexistence curve", which displays, for each value of T , the coexisting concentrations appropriate to the upper and lower phases.

Both the lambda line and the coexistence curve typical of a He^3 - He^4 mixture at saturated vapor pressure (SVP) are displayed in Fig. 1. In order to demonstrate the use of this diagram, consider a mixture of average concentration, $X=0.5$. Following

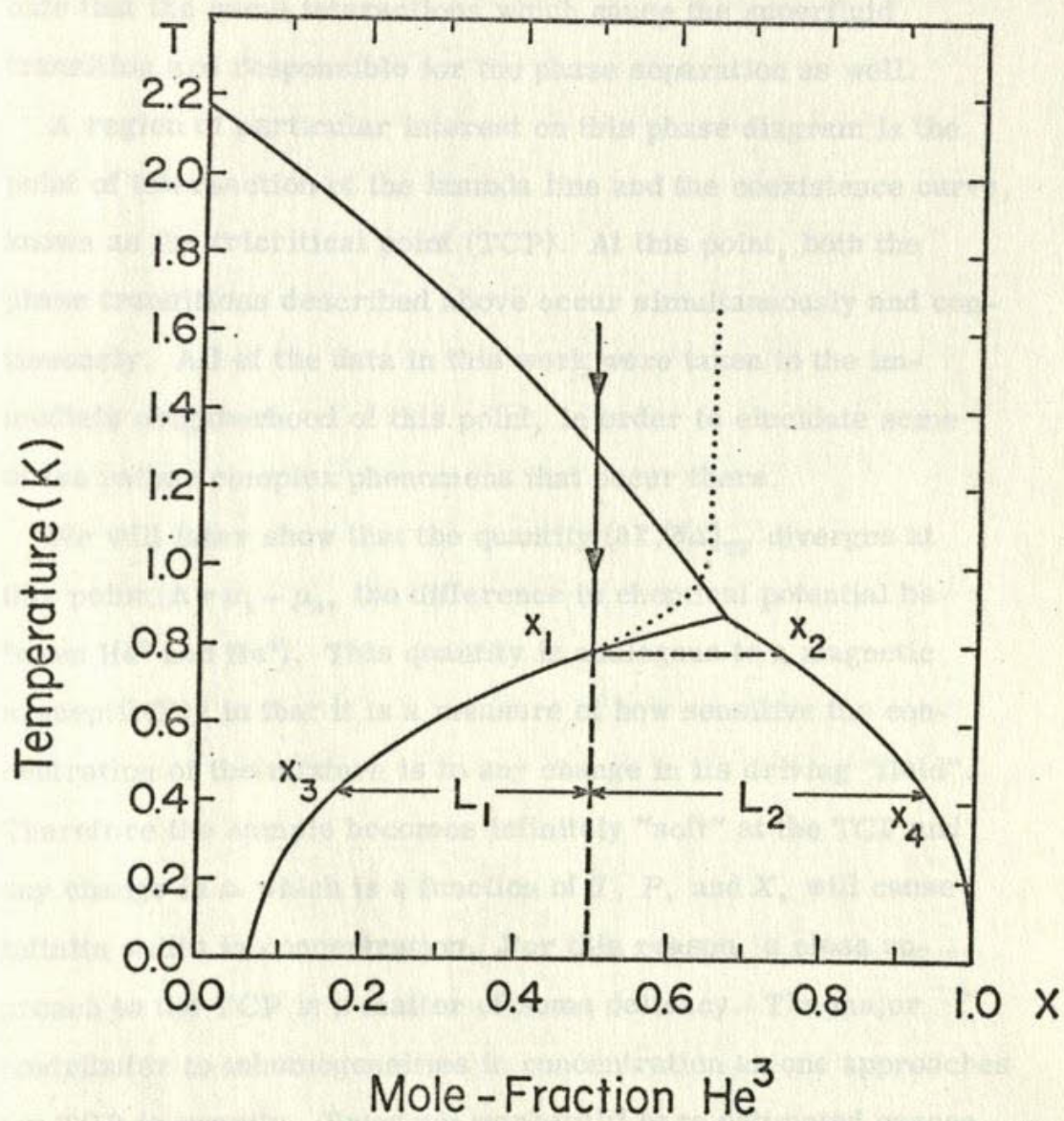
down the solid line marked (—●—), as temperature is lowered, we first encounter a lambda transition at $T_\lambda = 1.3$ K at which the entire sample becomes superfluid. Upon further cooling, the sample begins to phase separate at $T_s = 0.8$ K into phases of concentrations X_1 and X_2 . At some lower temperature, $T = 0.4$ K, phases of concentrations X_3 and X_4 coexist in relative amounts given by the ratio of the lengths L_2 and L_1 respectively. Note that at $T = 0$ K some He^3 remains dissolved in the He^4 . This is a result of the Fermi statistics of He^3 and is the basis for the operation of the He^3 dilution refrigerator.

Many systems are known that display one or the other of these two types of phase transition. Higher-order transitions displaying similar specific heat curves occur in binary alloys.¹ Many mixtures of organic liquids, including phenol and water, have a range of temperatures over which they are not mutually soluble in all proportions. However, systems that display both phenomena in this manner are quite rare. In particular, only a few anisotropic antiferromagnetic materials such as FeCl_2 and dysprosium aluminum garnet³ have phase diagrams similar to those of He^3 - He^4 mixtures.

It is reasonable to infer from Fig. 1 that these two phase transitions are, in fact, closely related phenomena. The coexistence curve shows an angular peak at $X \cong 0.67$ at which point the lambda line terminates exactly. This intersection divides the coexistence curve into the so called left-hand and right-hand branches. The

Figure 1

The $\text{He}^3 - \text{He}^4$ phase diagram under SVP



usual coexistence curves for binary mixtures have rounded tops much closer to $X=0.50$.⁴ It will come as no surprise, then, when phenomenological model calculations for this system indicate that the same interactions which cause the superfluid transition are responsible for the phase separation as well.

A region of particular interest on this phase diagram is the point of intersection of the lambda line and the coexistence curve, known as the tricritical point (TCP). At this point, both the phase transitions described above occur simultaneously and continuously. All of the data in this work were taken in the immediate neighborhood of this point, in order to elucidate some of the rather complex phenomena that occur there.

We will later show that the quantity $(\partial X / \partial \Delta)_{\text{TP}}$ diverges at this point ($\Delta = \mu_3 - \mu_4$, the difference in chemical potential between He^3 and He^4). This quantity is analogous to a magnetic susceptibility in that it is a measure of how sensitive the concentration of the mixture is to any change in its driving "field". Therefore the sample becomes infinitely "soft" at the TCP and any change in Δ which is a function of T , P , and X , will cause infinite shifts in concentration. For this reason, a close approach to the TCP is a matter of some delicacy. The major contributor to inhomogeneities in concentration as one approaches the TCP is gravity. Previous workers^{5,6} have estimated concentration gradients in excess of 1% over a height of 1 cm. in the lower phase at the TCP. Since the exact magnitude and the form

of this gradient were not known, it became difficult to extend the left and right hand branches of the coexistence curve into the immediate neighborhood of the TCP. Indeed, the concentration at a given height in the sample chamber might follow a path in T - X space like the one shown by the line of points in Fig. 1, skirting entirely around the TCP and not joining the true coexistence curve for 10 mK below the TCP.

The original motivation for this work was to determine the magnitude and the functional form of the gravitationally induced concentration gradient near the TCP in order to determine the phase diagram more precisely and completely. We simultaneously hoped that this information would also make possible a determination of $(\partial X/\partial \Delta)_{\text{TP}}$ to sufficient precision to make a quantitative statement about its limiting behavior as the TCP is approached.

This asymptotic behavior can be described in the scaling hypothesis (to be discussed later) by a parameter δ defined as:

$$\left(\frac{\partial X}{\partial \Delta}\right)_{\text{TP}} \propto (X - X_c)^{-(\delta-1)} \quad (1.1)$$

Here we introduce the subscript c as indicative of the value of a variable at the TCP. δ is the "critical exponent" associated with the singular behavior of the concentration susceptibility near this point. Some justification for the case of Eq. (1.1), as well as proof of the relationship between the gravitationally

induced concentration gradient and $(\partial X/\partial \Delta)_{TP}$ will be given in section III.

The remainder of this work will be organized as follows: In section II we will consider the prior experimental investigation of the region near the TCP. In section III a number of phenomenological models will be presented. Their predictions will be compared with the previously discussed experimental results, and efforts will be made to extract the predicted tricritical behavior for $(\partial X/\partial \Delta)_{TP}$. In section IV the apparatus employed in this work will be described. The procedures used to extract data as well as the data itself, will be presented and analysed in section V. Section VI is reserved for a summary and conclusion.

II. Previous Experimental Work

The complex behavior of He^3 - He^4 mixtures has been under investigation for nearly thirty years. Abraham, Weinstock and Osborne⁷ observed the lambda line from $X=0$ to $X=0.28$ in 1949 by measuring the flow rate of a sample through a superleak as a function of temperature. The existence of a coexistence curve was demonstrated by Walters and Fairbank⁸ in 1956. They employed a nuclear magnetic resonance technique to observe the He^3 line with sensing coils at the top and bottom of their apparatus. Subsequently, both the lambda line and the coexistence curve were explored by a variety of methods. Daunt and Heer⁴¹ used the heat leak through a sample filled capillary to locate the superfluid transition while Dash and Taylor⁴² employed an oscillating disk viscosimeter for the same purpose. Peshkov and Zinov'eva⁴³ observed the coexistence curve optically while Roberts and Sydoriak obtained data from observation of discontinuities in the temperature derivative of first sound velocities. De Bruyn Ouboter *et al.*⁴⁵ determined the coexistence curve by using specific heat measurements. While this list of experiments is certainly not complete, it gives some idea of the wide variety of methods available to the experimenter in this field. The shape of the top of the coexistence curve and its intersection with the lambda line was first accurately determined by Graf, Lee and Reppy⁹ in 1967. They used a capacitive

technique identical to the one employed in this experiment to determine the concentrations of the upper and lower phases. The lambda transition was detected by qualitative measurements of the thermal relaxation time. Many other experimenters have contributed greatly to this field of knowledge. A review of this early work can be found in Taconis and DeBruyn Ouboter¹⁰ and Peshkov.¹¹

Subsequently, several experiments were done which measured the effects of pressure upon the phase diagram and explored the region near the TCP in great detail. Notably Zimmermann¹² *et al.* employed specific heat measurements at SVP to determine C_{px} , $C_p\Delta$, Δ and $(\partial X/\partial \Delta)_{TP}$ over the ranges $0.53 \leq X \leq 0.73$ and $0.6 \text{ K} \leq T \leq 1.4 \text{ K}$. Goellner and Meyer¹³ measured the vapor pressure of He³-He⁴ mixtures over a similar range of temperature and concentration. From this data they obtained values for Δ and $(\partial X/\partial \Delta)_{TP}$ and investigated the critical behavior of these quantities near the TCP. Watts and Webb^{6,14} used light scattering from the critical opalescence of He³-He⁴ mixtures near the TCP to directly determine $(\partial X/\partial \Delta)_{TP}$. Again, the critical behavior of this quantity was investigated. The gravitationally induced concentration gradient also was measured by an interferometric technique, and was determined to have resulted in a decrease in X of 0.005 ± 0.002 at a distance 4mm below the interface between the two phases at T_c . Ahlers and Greywall^{15,16} have used careful second sound measurements

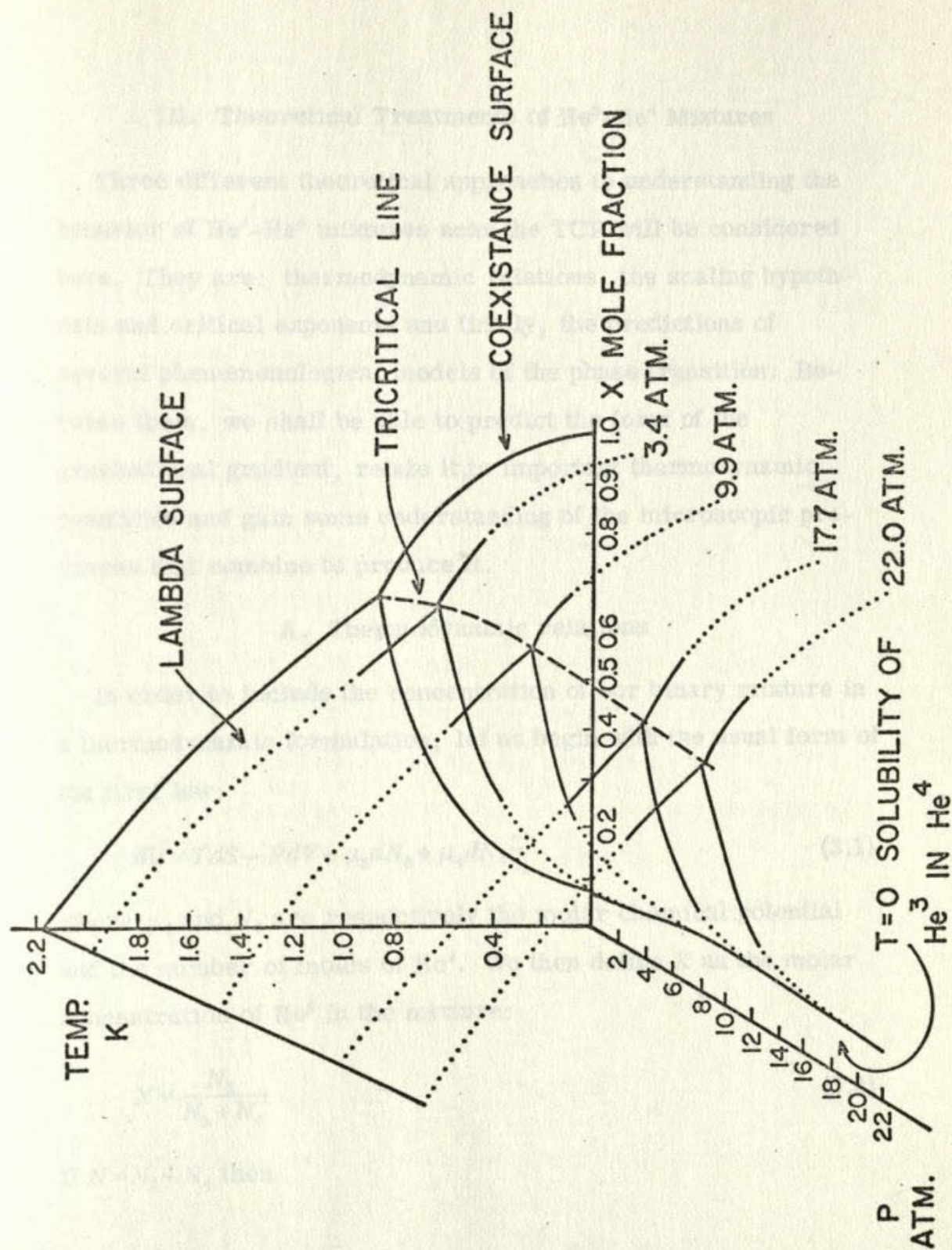
in the superfluid region near the TCP and along the left hand branch of the coexistence curve. The phase diagrams determined by these researches all agree tolerably well. Both Goellner and Meyer, and Zimmermann *et al.* also determine that the exponent δ has a value close to 2.

Away from SVP, Lai,¹⁷ Johnson¹⁸ and Rohde¹⁹ have explored the phase diagram over the range $0.35 \leq X \leq 0.80$ at pressure varying from SVP to 22 atm. - near the solidification point - using the same techniques as Graf, Lee and Reppy. A composite of their data is shown in Fig. 2. Note that the essential feature of the phase diagram remains: the lambda line stays firmly rooted in the angular peak of the coexistence curve. The TCP itself shows interesting behavior, T_c decreasing monotonically with increasing P while X_c first increases with increasing P up to ~ 9.9 atm. and then decreases with increasing P until the solidification point is reached. It should be noted that the $T=0$ solubility of He^3 in He^4 as measured by Watson, Richardson and Reppy²⁰ shows qualitatively similar behavior.

Near the TCP the results of all these experiments show the effect of the presence of gravitationally induced concentration gradients. Attempts have been made to correct for the "broadening" of thermodynamic functions and the deviations in concentration by estimating - or in the case of Watts and Webb, directly measuring - the gradient.

Figure 2

The pressure dependence of the $\text{He}^3 - \text{He}^4$ phase diagram



III. Theoretical Treatments of He³-He⁴ Mixtures

Three different theoretical approaches to understanding the behavior of He³-He⁴ mixtures near the TCP will be considered here. They are: thermodynamic relations, the scaling hypothesis and critical exponents and finally, the predictions of several phenomenological models of the phase transition. Between them, we shall be able to predict the form of the gravitational gradient, relate it to important thermodynamic quantities and gain some understanding of the microscopic processes that combine to produce it.

A. Thermodynamic relations

In order to include the concentration of our binary mixture in a thermodynamic formulation, let us begin with the usual form of the first law:

$$dU = TdS - PdV + \mu_3 dN_3 + \mu_4 dN_4 \quad (3.1)$$

where μ_i and N_i are respectively the molar chemical potential and the number of moles of Heⁱ. We then define X as the molar concentration of He³ in the mixture:

$$X = \frac{N_3}{N_3 + N_4} \quad (3.2)$$

If $N = N_3 + N_4$ then

$$\begin{aligned} N_3 &= NX \\ N_4 &= N(1 - X) \end{aligned} \quad (3.3)$$

So that:

$$dU = TdS - PdV + (\mu_3 - \mu_4)NdX \quad (3.4)$$

If we divide through by N , and define a chemical potential difference by:

$$\Delta = (\mu_3 - \mu_4) \quad (3.5)$$

we arrive at:

$$du = Tds - Pdv + \Delta dX \quad (3.6)$$

where lower case variables indicate quantities per mole.

Note the close analogy with magnetic systems in which a term HdM appears in the first law. In this case we have a "field" Δ that drives changes in concentration rather than a field H doing the same for the magnetic moments of a system.

Let us now define the molar Gibbs potential of the system:

$$G = u - Ts + Pv \quad (3.7)$$

So that:

$$dG = -sdT + vdP + \Delta dX \quad (3.8)$$

This Gibbs potential must be a concave up function of concentration at all physically accessible points i.e.:

$$\left(\frac{\partial^2 G}{\partial X^2}\right)_{\text{TP}} = \left(\frac{\partial \Delta}{\partial X}\right)_{\text{TP}} \geq 0 \quad (3.9)$$

because a negative value for $(\partial \Delta / \partial x)_{\text{TP}}$ leads to instabilities in concentration just as a positive value of compressibility makes mechanical equilibrium impossible. We can similarly show that the Helmholtz free energy is concave up, i.e. that $(\partial \Delta / \partial x)_{\text{TV}} \geq 0$.

Since we know that a phase separation does occur in $\text{He}^3\text{-He}^4$ mixtures, we may infer that the Gibbs potential looks something like Fig. 3. For $T > T_c$, $G(x)$ must be concave up for all values of X . For $T < T_c$ there must be a "forbidden region" corresponding to the interior of the coexistence curve, for which $G(x)$ is concave down. This is the region between B and C on the lower curve. The concentration of the upper and lower phases is found by a bitangent construction (solid line) which minimizes the total Gibbs energy of the system. From the nature of this construction it is apparent that:

$$\left(\frac{\partial G}{\partial x}\right)_l = \Delta_l = \left(\frac{\partial G}{\partial X}\right)_u = \Delta_u \quad (3.10)$$

So Δ is the same in both coexisting phases. Further, as T approaches T_c from below, the hump in the $G(x)$ curve must get smaller and smaller, at last becoming a point of inflexion when $X_l = X_u$, that is, at the TCP. This implies that:

$$\left(\frac{\partial^2 G}{\partial X^2}\right)_{\text{TP}} = \left(\frac{\partial \Delta}{\partial X}\right)_{\text{TP}} = 0 \text{ at the TCP.} \quad (3.11)$$

Figure 3

A possible Gibbs potential for He^3 - He^4 mixtures

Then the concentration susceptibility, which is the inverse of the above quantity, diverges at the TCP.

In order to include gravity in our system, we must take a vector limit at the μ_1 and μ_2 in Eq. (3.1). Applying a method due to Ginzburg¹⁰ let us define $\mu_1^g(T, P, X)$ as the molar chemical potential free of the influence of gravity. Then:

$$\mu_1(T, z) = \mu_1^g(T, P, X) + m_1 g z$$

where z is the gravitational weight of μ_1 as the molecular weight of μ_1 is the vertical height from some arbitrary reference point. Then:

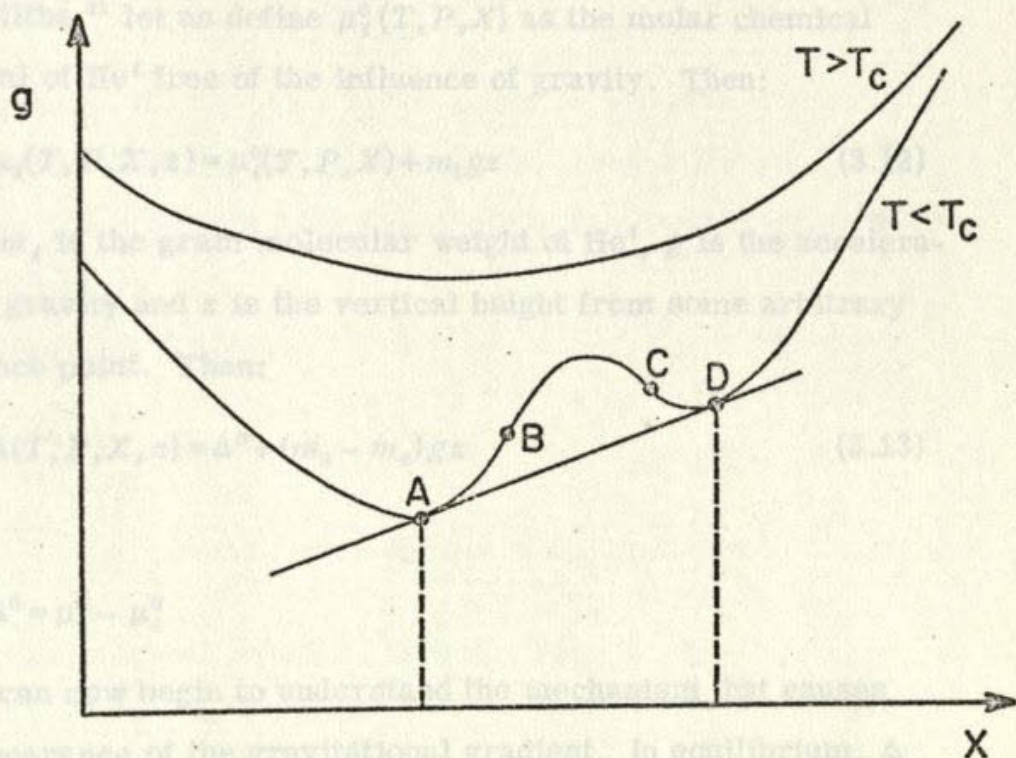
$$\Delta(T, z, X) = \mu_2(T, P, X) - \mu_1(T, P, X) - m_1 g z \quad (3.13)$$

with:

$$\Delta^0 = \mu_2 - \mu_1$$

We can now begin to understand the mechanism that causes

the appearance of the gravitational gradient. In equilibrium, Δ must be a constant throughout the sample. Were it not, it would force concentration changes in the sample, thus changing $\mu_1^g(T, X)$ until it became constant. Since Δ is constant in eq. (3.13) we have to assume that Δ^0 varies with height in such a way as to make the right hand side of that equation constant as well. As Δ^0 has no explicit dependence, its variation must be due to changes in X and P . T being a constant throughout the mixture at equilibrium. Thus including gravitational energies in our formulation



Thus the concentration susceptibility, which is the inverse of the above quantity, diverges at the TCP.

In order to include gravity in our system, we must take a closer look at the μ_3 and μ_4 in Eq. (3.1). Applying a method due to Griffiths,²¹ let us define $\mu_i^0(T, P, X)$ as the molar chemical potential of He^i free of the influence of gravity. Then:

$$\mu_i(T, P, X, z) = \mu_i^0(T, P, X) + m_i g z \quad (3.12)$$

where m_i is the gram molecular weight of He^i , g is the acceleration of gravity and z is the vertical height from some arbitrary reference point. Then:

$$\Delta(T, P, X, z) = \Delta^0 + (m_3 - m_4) g z \quad (3.13)$$

with:

$$\Delta^0 = \mu_3^0 - \mu_4^0.$$

We can now begin to understand the mechanism that causes the appearance of the gravitational gradient. In equilibrium, Δ must be a constant throughout the sample. Were it not, it would force concentration changes in the sample, thus changing $\mu_i^0(T, P, X)$ until it became constant. Since Δ is constant in eq. (3.13) we have to assume that Δ^0 varies with height in such a way as to make the right hand side of that equation constant as well. As Δ^0 has no explicit z dependence, its variation must be due to changes in X and P ; T being a constant throughout the mixture at equilibrium. Thus including gravitational energies in our formulation

of the first law has forced the appearance of a gravitational gradient in concentration.

Expressing the above idea in mathematical form:

$$0 \equiv \frac{d\Delta}{dz} = \left(\frac{\partial\Delta}{\partial z}\right)_{\text{TPX}} + \left(\frac{\partial\Delta}{\partial P}\right)_{\text{TXZ}} \frac{dP}{dz} + \left(\frac{\partial\Delta}{\partial X}\right)_{\text{TPZ}} \frac{dX}{dz} \quad (3.14)$$

This equation gives us a relationship between the concentration susceptibility $(\partial X/\partial\Delta)_{\text{TP}}$ and dX/dz , the gravitational gradient, since we can evaluate or estimate all other terms in the expression:

From eq. (3.13):

$$\left(\frac{\partial\Delta}{\partial z}\right)_{\text{TPX}} = (m_3 - m_4)g \quad (3.15)$$

$$\frac{dP}{dz} = -\rho g \quad \text{where } \rho = \text{the density of the mixture}^* \quad (3.16)$$

and from a Maxwell relation (Appendix B):

$$\left(\frac{\partial\Delta}{\partial P}\right)_{\text{TX}} = \left(\frac{\partial v}{\partial X}\right)_{\text{TP}} \quad (3.17)$$

giving:

$$\left(\frac{\partial X}{\partial\Delta}\right)_{\text{TP}} = \frac{dX/dz}{g[(m_4 - m_3) + \rho(\partial v/\partial X)_{\text{TP}}]} \quad (3.18)$$

Note that we have suppressed the "z-held-constant" subscript

*We will show in Appendix A that the approximation of constant density is a very good one.

for clarity in this and subsequent thermodynamic relations. It will be understood that all subsequent thermodynamic derivatives will be taken at constant z or, equivalently, have their gravity-free values. The denominator of the right hand side of eq. (3.18) contains only well behaved functions. Therefore the critical behavior of the concentration susceptibility is mirrored in the behavior of the gravitationally induced concentration gradient.

B. The Scaling Hypothesis

The initial justification for the scaling hypothesis is experimental. It was noticed that sufficiently close to a critical point, the pairwise relationships between many suitably reduced experimental quantities could be expressed as power laws. For instance, if we choose the reduced temperature, t

$$t = \frac{T - T_c}{T_c} \quad (3.19)$$

as our independent variable, and express some other thermodynamic quantity as $f(t)$, then the limit:

$$\lim_{t \rightarrow 0} \frac{\ln f(t)}{\ln t} \equiv \lambda \quad (3.20)$$

gives us the *critical exponent* λ . The implication is that sufficiently close to T_c

$$f(t) \propto t^\lambda \quad (3.21)$$

This would be discovered experimentally by measuring f as a function of t close to $t=0$ and plotting the result on a log-log graph. If the data lay on a straight line as $t \rightarrow 0$, then the slope of this line would be the critical exponent for those two variables. An example of this process is shown in Fig. 4 in which the relationship between reduced density and temperature is explored near the gas-liquid critical point of He^4 .

In more formal mathematical terms, the scaling hypothesis can give us the functional forms of $(\partial X/\partial \Delta)_{\text{TP}}$ and, hence, dX/dz as we near the TCP. We first define a generalized homogeneous function:

$F(x, y)$ is homogeneous if:

$$F(\lambda^a x, \lambda^b y) = \lambda F(x, y) \quad (3.22)$$

$F(x, y)$ is said to be homogeneous in x to degree " a " and homogeneous in y to degree " b ". All homogeneous functions may be transformed by a suitable choice of λ to:

$$F(x, y) = x^a f'(y/x^b); \quad \lambda = \frac{1}{x} \quad (3.23)$$

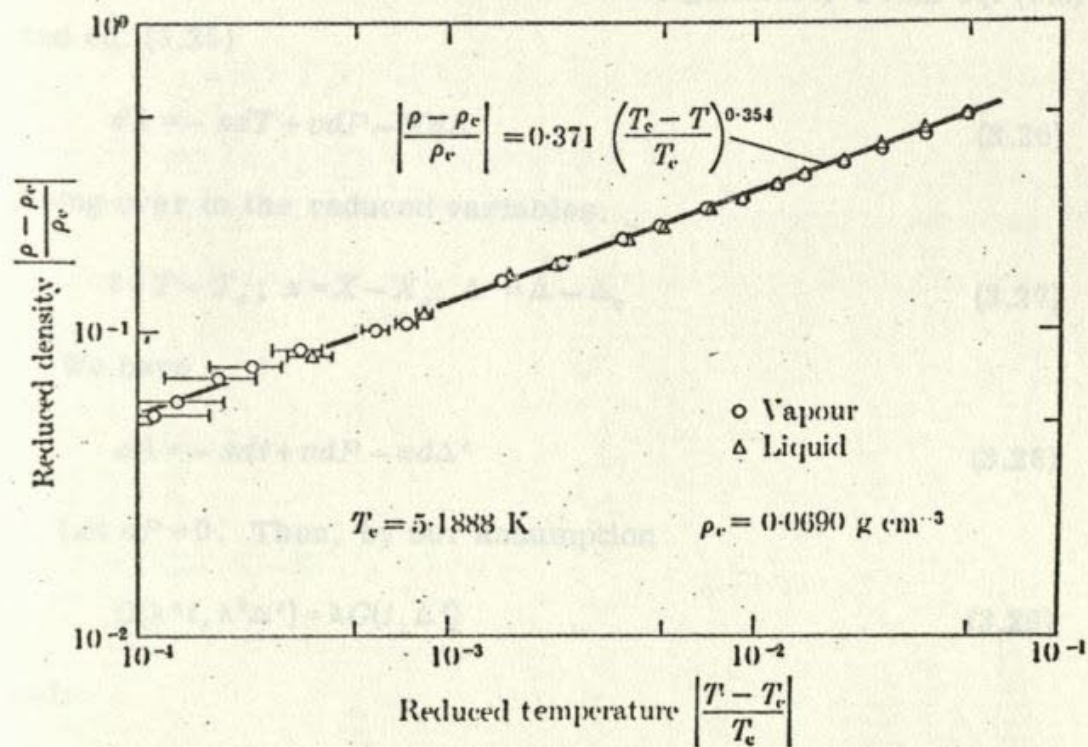
$$F(x, y) = y^b f''\left(\frac{x}{y^a}\right); \quad \lambda = \frac{1}{y} \quad (3.24)$$

These relations will be useful in defining critical exponents.

The scaling hypothesis then becomes the assumption that near the point of interest, the singular parts of the appropriate thermodynamic potential are generalized homogeneous functions of

Figure 4

Measurements of the coexistence curve for the liquid-vapor phase transition in He^4 near its critical point. After Roach³⁶ (1968). The critical exponent $\beta = 0.354$



the thermodynamic fields. In particular, let us assume that the potential:

$$A = u - T_s + Pv - \Delta X \quad (3.25)$$

is homogeneous. (Then all other potentials related to this one by Legendre transformations are also homogeneous.) From eq. (3.6) and eq. (3.25)

$$dA = -sdT + v dP - X d\Delta \quad (3.26)$$

Going over to the reduced variables:

$$t = T - T_c; \quad x = X - X_c; \quad \Delta' = \Delta - \Delta_c \quad (3.27)$$

We have

$$dA = -s dt + v dP - x d\Delta' \quad (3.28)$$

Let $dP = 0$. Then, by our assumption

$$G(\lambda^a t, \lambda^b \Delta') = \lambda G(t, \Delta') \quad (3.29)$$

and:

$$\lambda^b \frac{\partial G(\lambda^a t, \lambda^b \Delta')}{\partial \Delta'} = \lambda \frac{\partial G(t, \Delta')}{\partial \Delta'} \quad (3.30)$$

so:

$$\lambda^b x(\lambda^a t, \lambda^b \Delta') = \lambda x(t, \Delta') \quad (3.31)$$

if we set $\lambda = t^{-1/a}$ and explore the limit as $t \rightarrow 0$ along $\Delta' = 0$ we get

$$(t^{-1/a})^{b-1} x(1, 0) = x(t, 0) \quad (3.32)$$

and we see that:

$$\lim_{\substack{t \rightarrow 0 \\ \Delta' = 0}} x(t, 0) \sim t^{1-b/a} \quad (3.33)$$

by the usual definition of critical exponents

$$(X - X_c) \propto |T - T_c|^\beta \quad (3.34)$$

and we can make the identification $\beta = (1 - b)/a$.

Similarly, by setting $\lambda = \Delta'^{-1/b}$, and proceeding as above to determine the behavior as $\Delta' \rightarrow 0$ along $t=0$ we can get the relation:

$$\lim_{\substack{\Delta' \rightarrow 0 \\ t=0}} x(t, 0) \sim \Delta'^{1-b/b} \quad (3.35)$$

and comparing this to the usual:

$$(X - X_c)^\delta \propto (\Delta - \Delta_c) \quad (3.36)$$

we see:

$$\delta = \frac{b}{1-b} \quad (3.37)$$

By choosing other values for λ and taking other differentiations, the other usual critical exponents may be expressed in terms of a and b , and thus, finally, in terms of one another. The results of these calculations, as well as the definitions of the

usual critical exponents are summarized below in table (3.1).

Table 3.1

<u>Exponent</u>	<u>Definition</u>
γ	$\left(\frac{\partial X}{\partial \Delta}\right)_{TP} \propto T - T_c ^{-\gamma}$
β	$(X - X_c) \propto T - T_c ^\beta$
δ	$(\Delta - \Delta_c) \propto (X - X_c)^\delta$
	or
	$\left(\frac{\partial X}{\partial \Delta}\right)_{TP} \propto (X - X_c)^{-(\delta-1)}$
α	$C_p = T \left(\frac{\partial S}{\partial T}\right)_{TP} \propto T - T_c ^{-\alpha}$

Relations:

$$\begin{aligned}\gamma &= \beta(\delta - 1) \\ \alpha + z\beta + \gamma &= Z\end{aligned}$$

Another justification for the scaling hypothesis is that many of the relationships between the critical exponents, such as those in table 3.1, above, can be derived as *inequalities* by rigorous thermodynamic argument. Also, as we shall see, many theories give us thermodynamic results that "scale".

We are now in a position to say something about the functional form of the gravitationally induced concentration gradient. If, as we suggest:

$$\left(\frac{\partial X}{\partial \Delta}\right)_{\text{TP}} \propto |X - X_c|^{-(\delta-1)}$$

and dX/dZ parallels this behavior then:

$$(X - X_c)^\delta \propto (z - z_c) \quad (3.38)$$

where z_c would be the height at which the tricritical concentration occurs. This implies that a careful determination of the functional relation between $(X - X_c)$ and $(z - z_c)$ would not only give us values for $(\partial X/\partial \Delta)_{\text{TP}}$ but would allow us to determine the critical exponent δ as well.

We will now consider the detailed prediction of several model calculations. Interest will be focused on how well the model reproduces the phase diagram of He^3 - He^4 mixtures, the extent to which behavior induced by changes in pressure is portrayed correctly, and the value provided by the model for the critical exponent δ .

C. The Hard-Sphere Fermi-Bose Mixture

The first model we will consider is that of a mixture of fermions and bosons with only hard-sphere interactions between the particles. This model was developed by van Leeuwen and Cohen²² in 1968 and further elucidated by Kincaid and Cohen²³ in 1975. Specifically they considered an anisotropic binary mixture of N_B hard-spheres of zero spin with mass m_B and diameter a mixed with N_F hard-spheres of spin $\frac{1}{2}$ with mass m_F and diameter

a. This approximates the interatomic repulsive interactions by a hard-sphere potential and ignores any attractive interactions between helium atoms. As a result of these approximations it was later found necessary to apply a temperature-dependent external pressure to the system so that its density would remain comparable to that of an isotopic helium mixture in similar circumstances.

The Hamiltonian considered was:

$$H = H_0 + H_1 \quad (3.39)$$

with:

$$H_0 = - \sum_{i=1}^{N_B} \frac{\hbar^2}{2m_B} \nabla_i^2 - \sum_{j=1}^{N_F} \frac{\hbar^2}{2m_F} \nabla_j^2 \quad (3.40)$$

and

$$H_1 = \frac{1}{2} \sum_{i \neq i'}^{N_B} \phi_{BB}(\vec{r}_i - \vec{r}_{i'}) + \frac{1}{2} \sum_{j \neq j'}^{N_F} \phi_{FF}(\vec{r}_j - \vec{r}_{j'}) \\ + \sum_{i=1}^{N_B} \sum_{j=1}^{N_F} \phi_{FB}(\vec{r}_i - \vec{r}_j) \quad (3.41)$$

Where H_0 is simply the Hamiltonian for a mixture of an ideal Bose and an ideal Fermi gas, and H_1 contains the various interaction energies between the bosons and the fermions. Since we are considering only hard sphere interactions, the various ϕ 's in H all have the property

$$\begin{aligned}\varphi &= 0 \text{ if } |r_1 - r_2| > a \\ \varphi &= \infty \text{ if } |r_1 - r_2| < a\end{aligned}\quad (3.42)$$

This Hamiltonian is solved using the pseudopotential method of Huang, Yang, and Lee²⁴. This involves the substitution of pseudopotentials of the form

$$\phi_{IJ} = 2\pi a \hbar^2 \left(\frac{1}{m_I} + \frac{1}{m_J} \right) \delta(\vec{r}_1 - \vec{r}_2); I, J = F, B \quad (3.43)$$

into H_1 . These forms were developed first by considering the two-body case and constructing a set of pseudopotentials that gave the correct energy levels. An N -body pseudopotential was then built up from the two-body pseudopotentials. The N -body pseudopotential, which has the sphere diameter " a " as an expansion parameter, is given only to first order in " a ".

The Hamiltonian is then solved by viewing H_1 as a perturbation on H_0 , and obtaining the energy levels, E_n , correct to order " a ". From these energy levels the partition function, and hence the free energy are calculated. Appropriate derivatives of the free energy, F , then give the quantities of interest:

$$\begin{aligned}\mu_F &= \left(\frac{\partial F}{\partial N_F} \right)_{TV} \\ \mu_B &= \left(\frac{\partial F}{\partial N_B} \right)_{TV} \\ P &= \left(\frac{\partial F}{\partial V} \right)_{T, N_F, N_B}\end{aligned}\quad (3.44)$$

The phase diagram is then calculated by identifying the condensation of the Bose component of the mixture with the onset of the superfluid transition in $\text{He}^3\text{-He}^4$ mixtures and mapping out the two phase region by setting the chemical potentials of the respective components in the upper and lower phases equal. As mentioned earlier, in order to compensate for the lack of attractive interactions, an external pressure has to be provided. A temperature-dependent pressure was chosen such that the density of the Bose component of the mixture was the same as that of He^4 liquid at 0K.

The results of these calculations appear in Fig. 5. The qualitative agreement between the experimentally determined values (dotted lines) and the theoretical calculations (solid lines) is remarkable, considering the relative simplicity of the assumptions of this model. The predictions of the model for the effects of pressure variation are, however, not good at all. They are summarized in the table below and compared with experimental determinations:

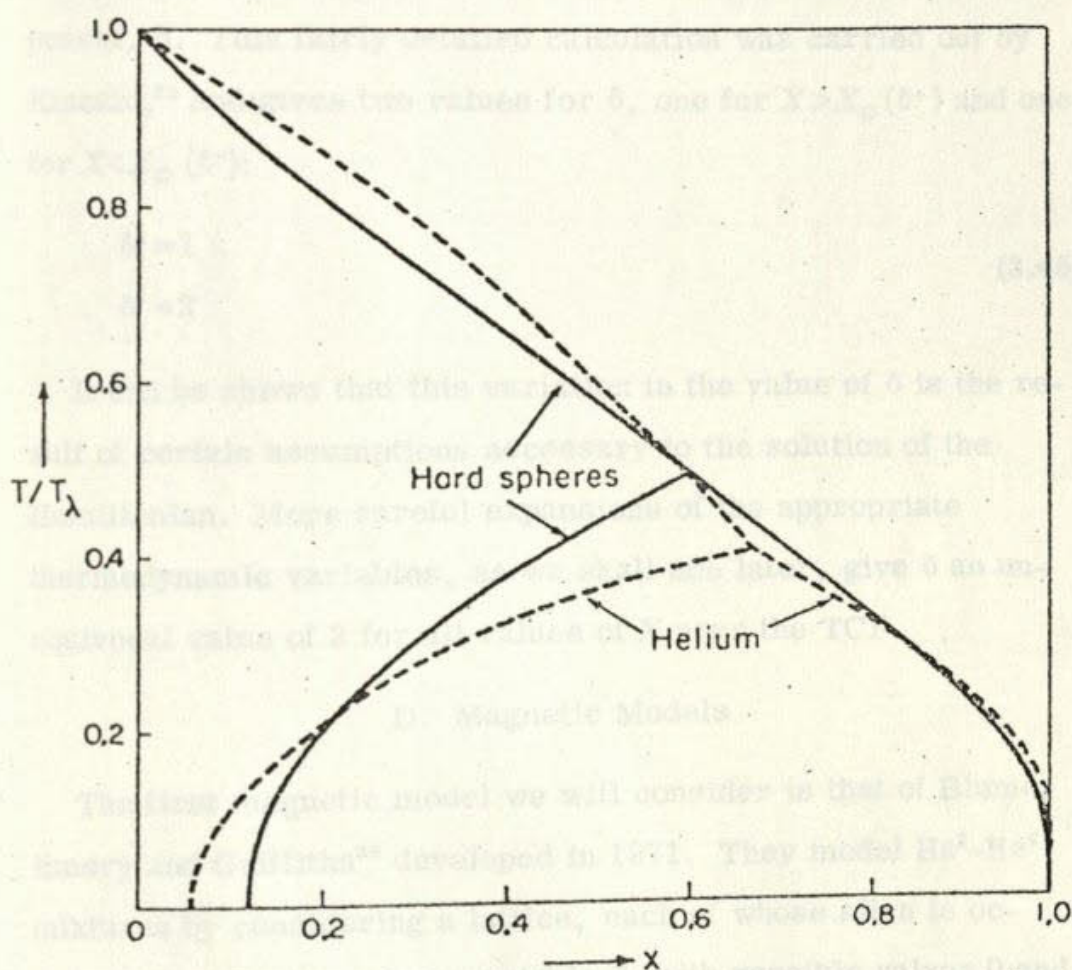
Table 3.2

As P increases:

<u>Hard Sphere Model</u>	<u>$\text{He}^3\text{-He}^4$ mixture</u>
T_λ increases	T_λ decreases
T_c/T_λ increases	T_c/T_λ first decreases, then increases
X_1 at $T = 0\text{K}$ decreases	X_1 at $T = 0\text{K}$ first increases, then decreases.

Figure 5

Phase diagram of the: Hard-Sphere Fermi-Bose Mixture model
together with the SVP helium phase diagram



This lack of agreement is hardly surprising considering that all attractive interactions, which might be expected to affect the behavior of the sample as the average interatomic distance varied, were neglected.

This model also supplies us with a value for the critical exponent, δ . This fairly detailed calculation was carried out by Kincaid,²⁵ and gives two values for δ , one for $X > X_c$ (δ^+) and one for $X < X_c$ (δ^-):

$$\begin{aligned}\delta^+ &= 1 \\ \delta^- &= 2\end{aligned}\tag{3.45}$$

It can be shown that this variation in the value of δ is the result of certain assumptions necessary to the solution of the Hamiltonian. More careful expansions of the appropriate thermodynamic variables, as we shall see later, give δ an unequivocal value of 2 for all values of X near the TCP.

D. Magnetic Models

The first magnetic model we will consider is that of Blume, Emery and Griffiths²⁶ developed in 1971. They model He³-He⁴ mixtures by considering a lattice, each of whose sites is occupied by a fictitious spin variable S_i with possible values 0 and ± 1 . A He³ atom at a particular site corresponds to the $S_i = 0$ state and a He⁴ atom to $S_i = \pm 1$. All sites are occupied by one atom of one type or the other. The spin associated with He⁴ is double valued to allow for the possibility of superfluid ordering. In fact,

the superfluid order parameter is defined as:

$$M = \frac{1}{N} \sum_{i=1}^N \langle S_i \rangle \quad \langle \rangle = \text{thermal average} \quad (3.46)$$

With $M=0$ indicative of normal fluid and $M \neq 0$ indicative of superfluid. The number of He^3 and He^4 atoms present is given by:

$$\begin{aligned} N_3 &= \sum_{i=1}^N (1 - S_i^2) \\ N_4 &= \sum_i S_i^2 \end{aligned} \quad (3.47)$$

and the He^3 concentration by:

$$X = \frac{\langle N_3 \rangle}{N} \quad (3.48)$$

If the system is translationally invariant, this gives:

$$M = \langle S_i \rangle \quad (3.49)$$

and

$$X = 1 - \langle S_i^2 \rangle \quad (3.50)$$

The Hamiltonian considered is:

$$H = H_S + H_I - \mu_3 \hat{N}_3 - \mu_4 \hat{N}_4 \quad (3.51)$$

where μ_3 and μ_4 are the chemical potentials of He^3 and He^4 and

$$H_s = -J \sum_{nn} S_i S_j \quad (3.52)$$

nn = summation over nearest neighbor pairs

Since this term in the Hamiltonian will lead to a second-order phase transition at which M spontaneously assumes a non-zero value, it is responsible for the "superfluid ordering" of the sample. In order to include the possibility of other sorts of interactions being responsible for the behavior of their model, the authors include an interaction term:

$$\begin{aligned} H_I = & -K_{33} \sum_{nn} (1 - S_i^2)(1 - S_j^2) - K_{44} \sum_{nn} S_i^2 S_j^2 \\ & - K_{34} \sum_{nn} [S_i^2 (1 - S_j^2) + S_j^2 (1 - S_i^2)] \end{aligned} \quad (3.53)$$

supplying different interaction energies if neighboring sites are occupied by He^3 - He^3 , He^3 - He^4 , or He^4 - He^4 pairs.

The total Hamiltonian is then rewritten:

$$H = -J \sum_{nn} S_i S_j - K \sum_{nn} S_i^2 S_j^2 + \Delta \sum_i S_i^2 - N(zK_{33} + \mu_3) \quad (3.54)$$

where:

$$R = K_{33} + K_{44} - 2K_{34}$$

$$\Delta = \mu_3 - \mu_4 + 2z(K_{33} - K_{34})$$

and:

z = number of nearest neighbors .

By varying the relative strengths of J and K , the types of phase diagram generated by an entirely "superfluid driven" system ($K=0, J \neq 0$), or that of a system whose behavior is entirely determined by the relative strengths of interaction between its constituents ($J=0, K \neq 0$), or that of any intermediate case, can be explored. The authors solve this Hamiltonian in the molecular field approximation and arrive at the following results for X and M :

$$(1-X) = \frac{2 \cosh \beta \mathcal{J} M}{\exp\{\beta[\Delta - \mathcal{K}(1-X)]\} + 2 \cosh \beta \mathcal{J} M} \quad (3.55)$$

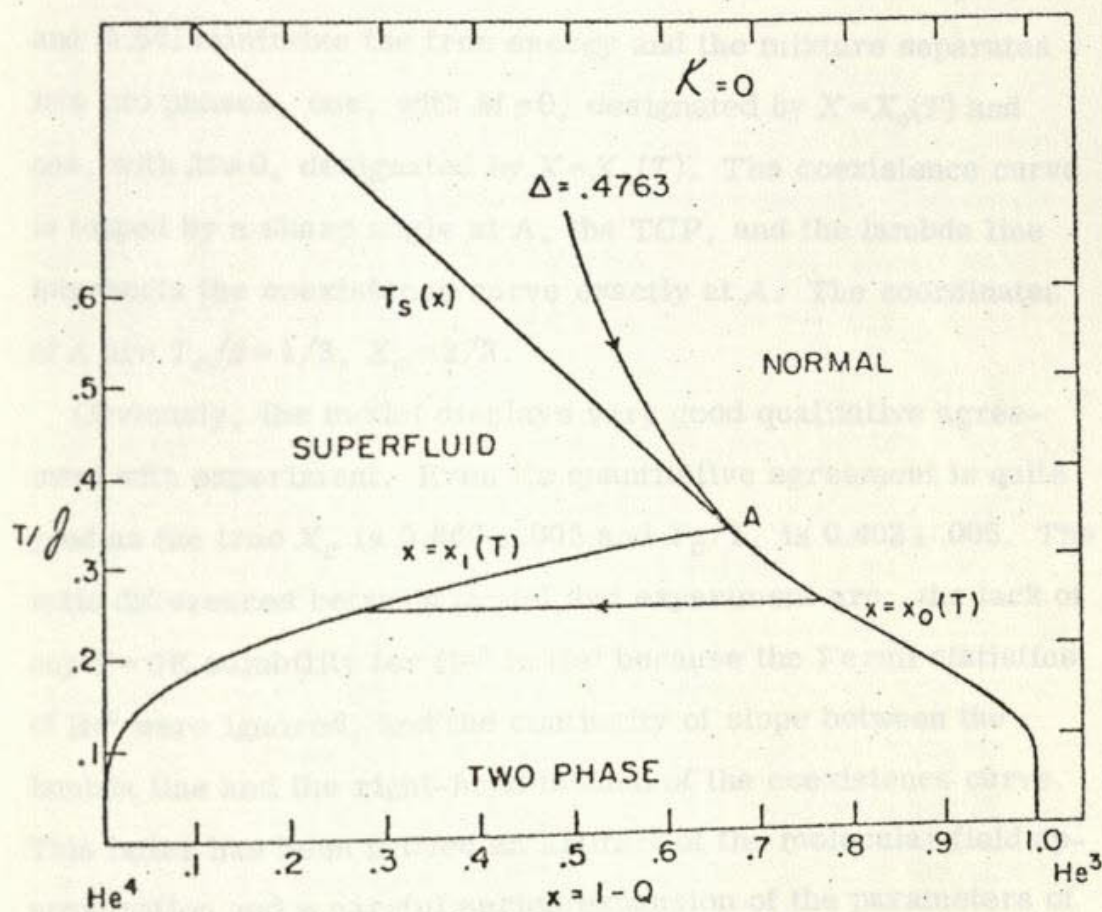
$$M = \frac{2 \sinh \beta M}{\exp\{\beta[\Delta - \mathcal{K}(1-X)]\} + 2 \cosh \beta \mathcal{J} M} \quad (3.56)$$

$$\begin{cases} \mathcal{J} = Jz \\ \mathcal{K} = Kz \\ \beta = (kT)^{-1} \end{cases}$$

In general, it is necessary to solve these self-consistent equations numerically, assuming values for $\mathcal{J}$, $\mathcal{K}$, and Δ . There may be several pairs of answers (M, X) for any given set of parameters, and those are chosen which minimize the free energy. Employing these methods, Blume, Emery and Griffiths explored the phase diagram for several ratios of $\mathcal{J}/\mathcal{K}$. Fortunately, the phase diagram that most resembles that of He^3 - He^4 mixtures occurs when $\mathcal{K} \cong 0$, thus uncoupling eqs. (3.55) and (3.56) and making their solution that much easier. A phase diagram with $\mathcal{K}=0$ is displayed in Fig. 6. A region of normal fluid with $M=0$,

Figure 6

The Blume, Emery and Griffiths²⁶ model phase diagram when $\mathcal{K}=0$. The reduced temperature axis is in units of T/J .



is separated from a region of superfluid ($M \neq 0$) by a lambda line, designated $T_s(x)$. In this model, the lambda line is straight, and given by:

$$T_s = \mathcal{J}(1 - X) \quad (3.57)$$

For $T/\mathcal{J}$ values below $1/3$, two sets of solutions to eqs. (3.55) and (3.56) minimize the free energy and the mixture separates into two phases, one, with $M=0$, designated by $X=X_0(T)$ and one, with $M \neq 0$, designated by $X=X_1(T)$. The coexistence curve is topped by a sharp angle at A , the TCP, and the lambda line intersects the coexistence curve exactly at A . The coordinates of A are $T_c/\mathcal{J} = 1/3$, $X_c = 2/3$.

Obviously, the model displays very good qualitative agreement with experiment. Even its quantitative agreement is quite good as the true X_c is $0.669 \pm .005$ and T_c/T_λ is $0.402 \pm .005$. The main differences between model and experiment are: the lack of any $T=0K$ solubility for He^3 in He^4 because the Fermi statistics of He^3 were ignored, and the continuity of slope between the lambda line and the right-hand branch of the coexistence curve. This latter has been proved an artifact of the molecular field approximation and a careful series expansion of the parameters of this model by Saul and Wortis²⁷ results in differing slopes for the lambda line and the right-hand side of the coexistence curve.

This model is not well suited for any determination of its pressure sensitivity. As all lattice sites are filled, no variations

in density are permitted, and no terms involving pressure or volume appear in the thermodynamic potentials. We will therefore later discuss a similar model due to Takagi that does permit lattice vacancies, and therefore a determination of its behavior at various densities.

We must finally make a determination of the value for the critical exponent, δ , predicted by this model. This is done explicitly from eqs. (3.55) and (3.56) in Appendix C with the result that $\delta^+ = 1$, $\delta^- = 2$, just as in the hard sphere model. These calculations also result in a functional form for Δ in terms of X near the TCP. We are thus able to calculate $(\partial\Delta/\partial x)_{TP}$ for various values of the adjustable parameters $\mathcal{J}$ and $\mathcal{K}$. Therefore, even though the calculation of an explicit pressure dependence is impossible in this model, it is tempting to adjust the above parameters so that T_C and X_C take on the values appropriate to different pressures. We might then hope that the concentration susceptibility calculated from these parameters will give some idea of the pressure dependence of the gravitational gradient. The result of such a procedure is that at a given value of $(X - X_C)$, $(\partial x/\partial\Delta)_{TP}$ increases as X_C increases. Remembering the experimental behavior of X_C as a function of pressure, this indicates that the gravitationally induced concentration gradient should be a maximum at $P \cong 9.9$ atm and decrease monotonically as the pressure moves away from that value. We will later discuss this prediction in the light of our experimental determinations.

The other magnetic model we will consider is that of Takagi²⁸. Outwardly similar to the Blume, Emery and Griffiths model, it is a generalization of the work of Matsubara and Matsuda²⁹, who dealt with a lattice model for pure He⁴. In order to incorporate the dynamics of the He³ without increasing the degrees of freedom of his model, Takagi treats the He³ as a classical gas "background", solves its dynamics separately, and includes its kinetic energy term as part of its chemical potential. This lack of parallelism in the treatment of He³ and He⁴ will cause us severe difficulties later, when we try to extract a value of Δ from this model.

In this model, again, we have a lattice, each of whose sites is occupied by a fictitious spin. The z components of these spins have the range of values: $-1, 0, 1$. The assignment of physical significance to these spin values is, however, very different than in the Blume, Emery and Griffiths model: $+1$ indicates a site occupied by He⁴; 0 , a vacant site; and -1 a site occupied by He³. This is not an Ising model in that the possibility of spin ordering in the $X - Y$ plane is not excluded. Indeed, it is just such an ordering that produces the superfluid transition. This assignment of spins leads, not surprisingly, to a very different Hamiltonian:

$$H = H_S + H_I + H_C \quad (3.58)$$

with:

$$H_s = -\frac{J}{2\gamma_0} \sum_{nn} S_i^z S_i^+ S_j^- S_j^z \quad (3.59)$$

$$H_I = -K \sum_{nn} (S_i^z)^2 (S_j^z)^2 - I \sum_{nn} S_i^z S_j^z - L \sum_{nn} (S_i^z)^2 S_j^z \quad (3.60)$$

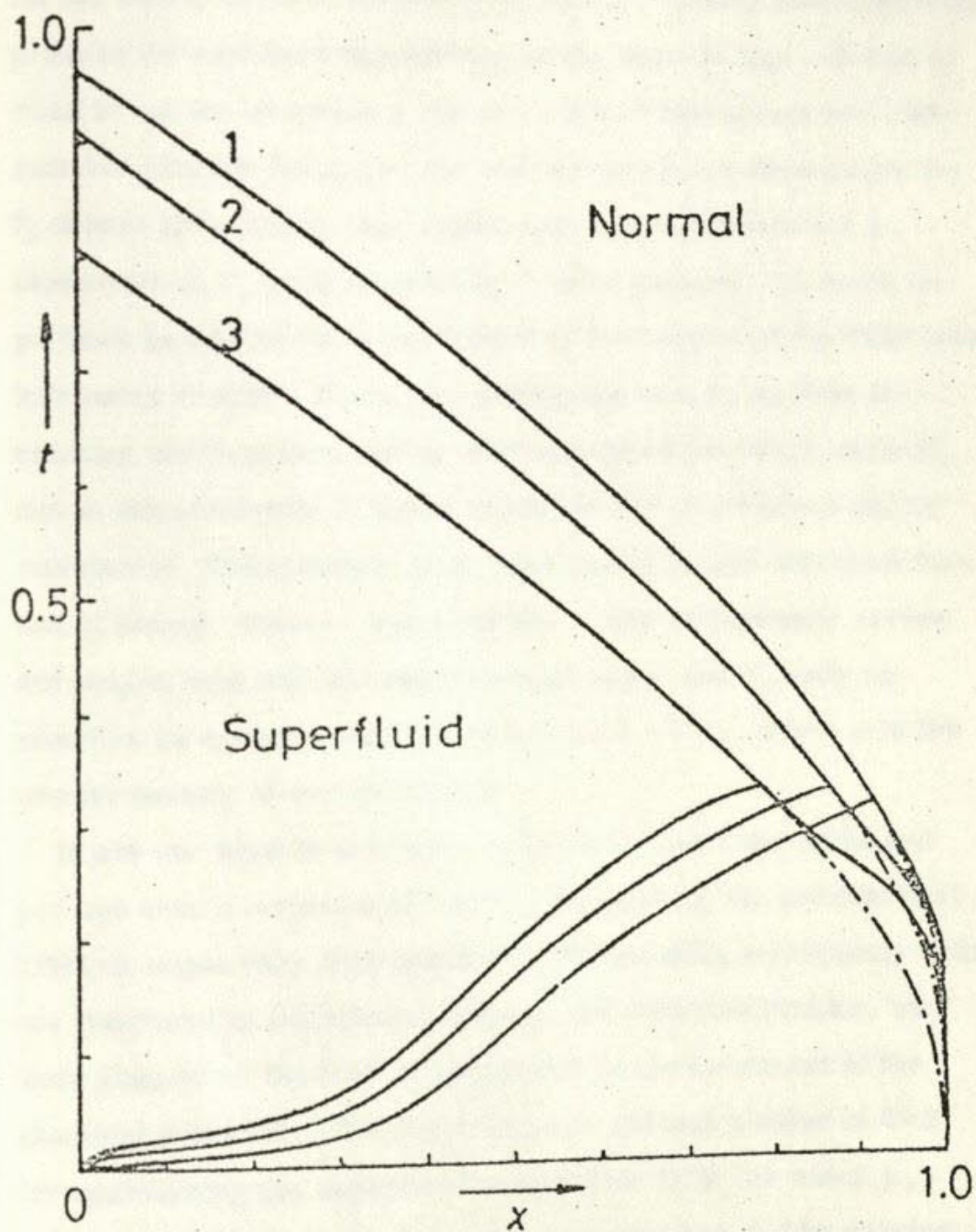
$$H_C = -H_1 \sum_j S_j^z - H_2 \sum_j (S_j^z)^2 \quad (3.61)$$

Where γ_0 is the number of nearest neighbors, K , I , and L are determined by the values of the various intraparticle potentials, and H_1 and H_2 are functions of the chemical potentials including a kinetic energy term for the He^3 . H_s is a superfluid ordering term resulting from the dynamics of He^4 . H_I is an interaction term whose coefficients are combinations of the potentials V_{ij} between He^i and He^j . H_C is a term that includes the effects of the chemical potentials of He^3 and He^4 . This Hamiltonian is first presented in second quantization formalism and then cast in the above form by demonstrating that the appropriate combinations of spin operators are, in fact, the creation, destruction, and number operators required. Unfortunately, before going on to solve this Hamiltonian, Takagi sets $H_I = 0$ and thus considers only superfluid driven effects on the phase diagram.

The results of these calculations are shown in Fig. 7, for various densities. Again, the qualitative features of the phase diagram are duplicated quite well. We again observe the continuity of slope between the lambda line and the right-hand branch of the coexistence curve, and the lack of solubility for

Figure 7

The phase diagrams of the Takagi²⁸ model for different lattice densities, ρ . Curves 1, 2 and 3 refer to $\rho=0.65$, 0.75 and 0.85, respectively. The reduced temperature axis is in units of $T/T_\lambda(X=0, \rho=\frac{1}{2})$



He³ in He⁴ at $T = 0\text{K}$ that occur for the same reasons as advanced for the Blume Emery and Griffiths model. Takagi also correctly predicts the pressure dependence of the lambda line-but this in itself is not too surprising, as the work of Matsubara and Matsuda had already displayed the correct pressure dependence for T_λ of pure He⁴. Thus, this model only had to provide for a depression in T_λ with increasing X to be correct. Of more importance is this model's prediction of the motion of the TCP with increasing density. Here, the prediction of a T_c at first increasing and then decreasing with increased pressure while X_c moves monotonically to lower values is not at all borne out by experiment. Quantatively also, this model is less effective than that of Blume, Emery and Griffiths. The coexistence curves are shaped less like the experimental ones, and X_c only approaches its correct range of values as $\rho \rightarrow 0.95$, where ρ is the number density of occupied sites.

It was our hope to extract a value of δ from this model and perhaps even a measure of how the strength of the gravitational gradient might vary with pressure. Proceeding analogously with our treatment of the Blume, Emery and Griffiths results, we were plagued by the lack of symmetry in the treatment of the chemical potentials. We did manage to extract a value of $\delta = 2$ for approaching the superfluid side of that TCP for which $\mu_4 = \frac{1}{2} J$ along a line on which μ_4 was kept equal to $\frac{1}{2} J$ by varying both ρ and X .

Siemann and Huber³⁰ have investigated the critical behavior of the Takagi model near the lambda line and the TCP. Employing a method of double-time Green's functions, they extract "classical" values for all of the critical exponents. In particular, $\delta=2$ in the "paramagnetic" (i.e. normal fluid) phase at the TCP along a line normal to the phase separation curve in $T - \Delta$ space. No determination is made of exponents in the superfluid phase, and the pressure dependence of $(\partial x / \partial \Delta)_{TP}$ is not investigated.

In order to remove the apparent discontinuity in δ predicted by the theories examined here, we refer to a paper by Riedel and Wegner³¹ who employ methods developed by Wilson³² to closely examine the region near the λ line and critical point of the Blume, Emery and Griffiths model. They believe that the major cause of such discrepancies is the difficulty in achieving discontinuous behavior in the derivatives of the thermodynamic potential, when the potential itself is an analytic function. They claim that the usual methods employed, going to the "thermodynamic limit" of infinite volume, while correct, makes it very difficult to properly extract the singular behavior of the system and hence the critical exponents. To overcome this, they employ a generalization of the "block" scaling picture developed by Kadanoff³³, extracting differential equations for the coupling constants and magnetic field appropriate to the "block" which lead, in a natural way, to the lack of analyticity of the partition function.

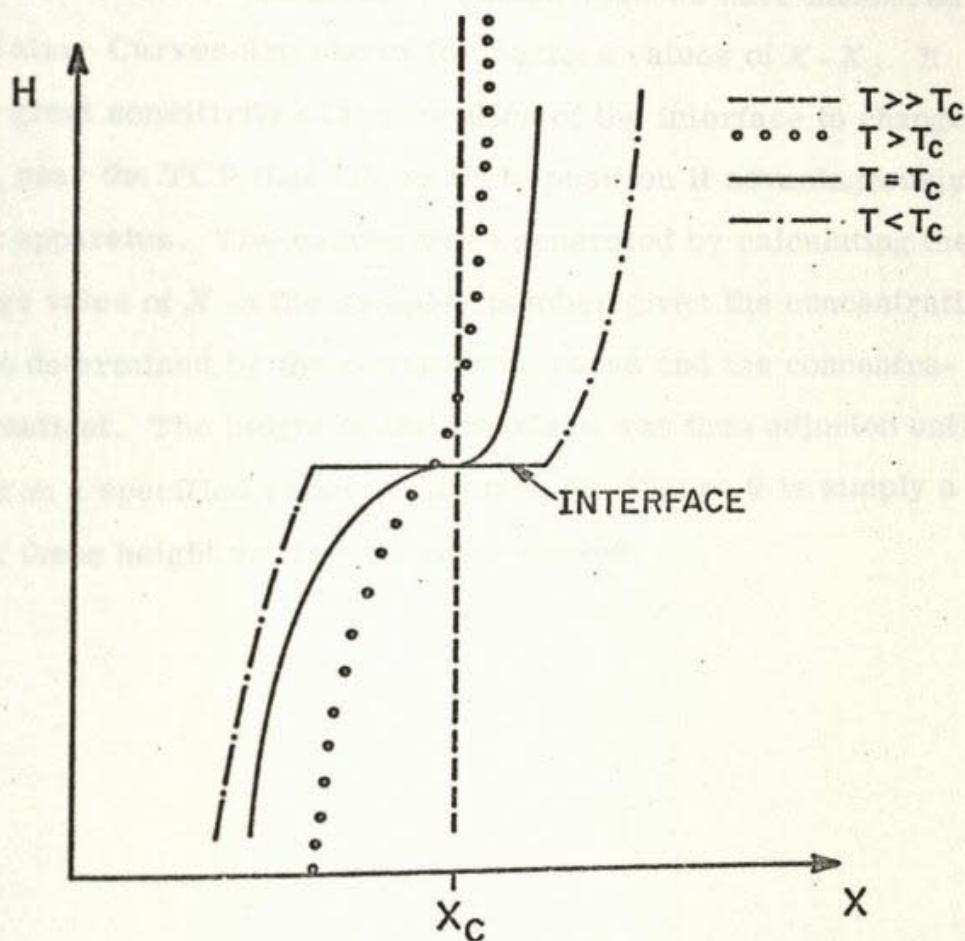
The process, as applied by Riedel and Wegner, involves a complex division and sectional integration over the phase space of the model and results in a constant value of 2 for δ on both sides of the TCP.

E. The Form of the Gravitationally Induced Concentration Gradient

Assuming that δ does indeed have the value 2, as both theory and experiment indicate, we can now show how the concentration gradient ought to behave in a real $\text{He}^3\text{-He}^4$ mixture as a function of temperature, Fig. 8. Assume that the average concentration of the mixture is X_C . Then for $T \gg T_C$ no appreciable gradient will be present. As $T \rightarrow T_C$, the gradient will begin to form, with a point of inflection at X_C . When $T = T_C$, parabolas with horizontal tangents at $X = X_C$ will form in both the upper and lower phases, with their common origin marking the incipient phase boundary. Finally, at $T < T_C$, the phase boundary is formed, and gravitational gradients exist in both the upper and lower phases. Note that now neither parabola displays a horizontal tangent as $(\partial\Delta/\partial x)_{\text{TP}} = 0$ only at the TCP. The gradient in the He^3 rich phase is shown as smaller than that in the He^4 rich phase since there is experimental evidence^{12,13,18,19} that it is less by about an order of magnitude. Our measurements have confirmed this. It should be mentioned that the behavior of a real $\text{He}^3\text{-He}^4$ mixture is more complicated than that portrayed in Fig. 8, because the average

Figure 8

A qualitative representation of the gravitationally induced concentration gradient in He^3 - He^4 mixtures at several temperatures



concentration of such a mixture is constant. Thus the height of the interface and the "incipient interface" is *not* constant. It is, in fact, a very strong function of the temperature, the magnitude of the concentration gradient, and the average concentration.

In Fig. 9 we display the motion of the interface for $T < T_c$ using the concentration gradient parameters we have measured at 2.5 atm. Curves are shown for various values of $X - X_c$. It is the great sensitivity of the location of the interface to changes $X - X_c$ near the TCP that allows us to position it advantageously in our apparatus. The curves were generated by calculating the average value of X in the sample chamber given the concentration profile determined by the coexistence curve and the concentration gradient. The height of the interface was then adjusted until X took on a specified value for a given T . Figure 9 is simply a plot of these height vs. temperature curves.

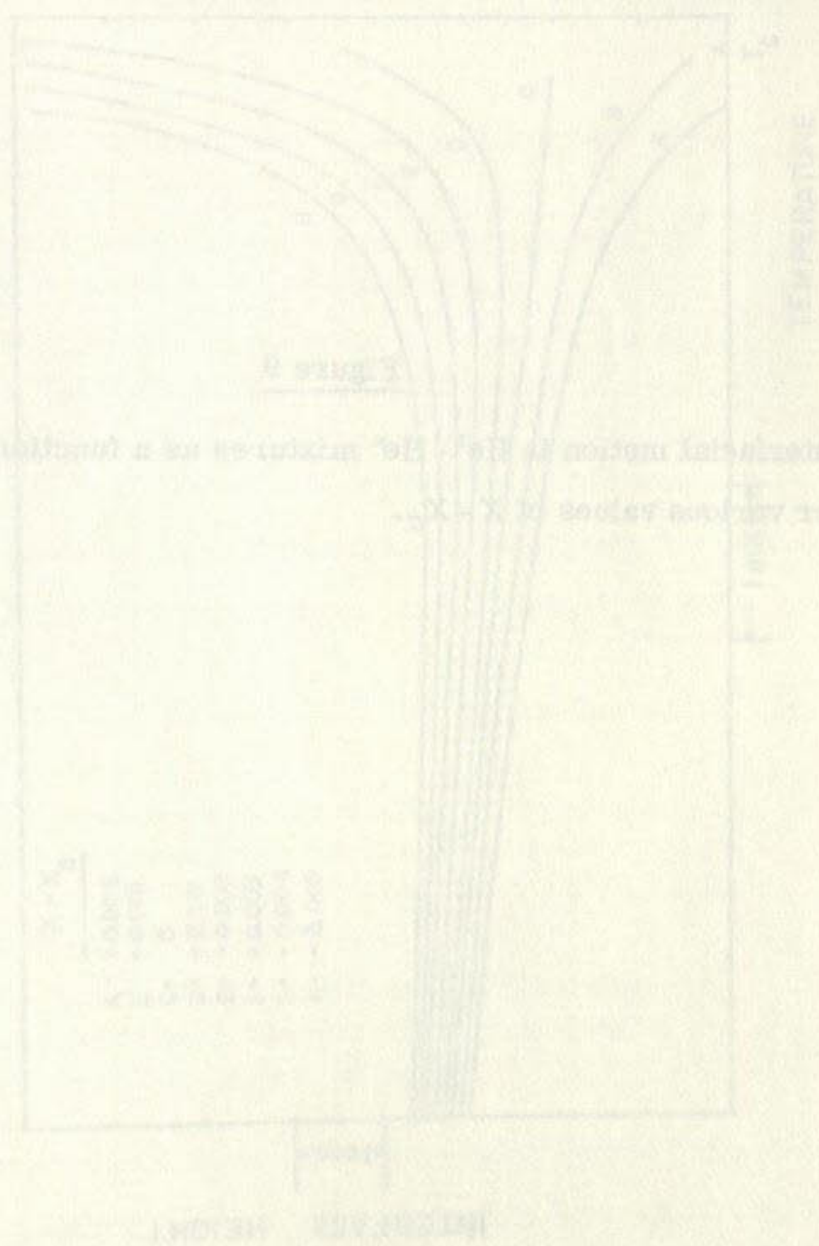
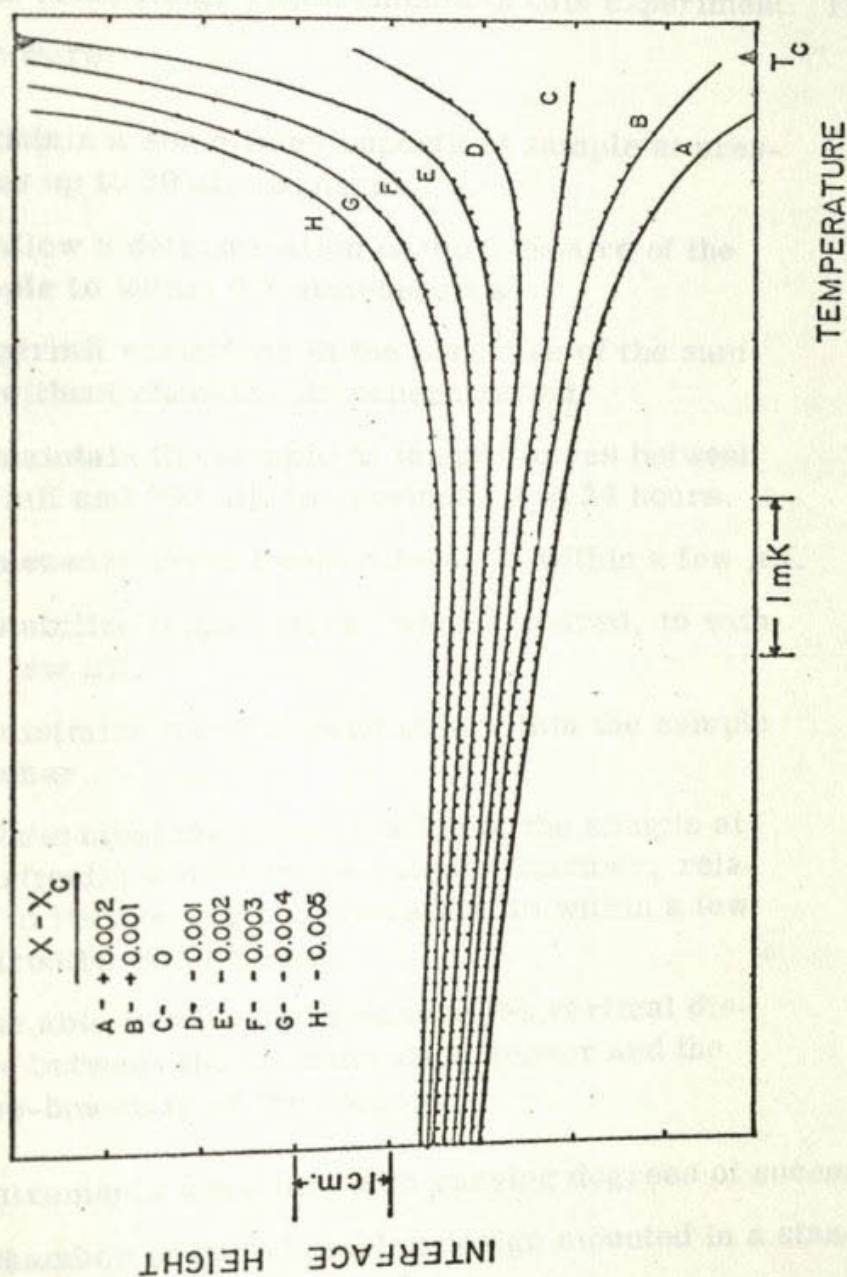


Figure 9

Interfacial motion in $\text{He}^3 - \text{He}^4$ mixtures as a function of $T - T_c$
for various values of $X - X_c$.

IV. Apparatus

A. General



IV. Apparatus

A. General

The design of this apparatus was an attempt to meet the various, often conflicting, requirements of this experiment. The requirements were:

1. To obtain a sometimes superfluid sample at pressures up to 30 atmospheres.
2. To allow a determination of the pressure of the sample to within 0.1 atmospheres.
3. To permit variations in the pressure of the sample without changing its concentration.
4. To maintain the sample at temperatures between 500 mK and 900 mK for periods up to 24 hours.
5. To measure these temperatures to within a few μK .
6. To stabilize temperature, when required, to within a few μK .
7. To minimize thermal gradients within the sample chamber.
8. To determine the concentration of the sample at a particular height in the sample chamber, relative to its average concentration, to within a few hundredths of a percent.
9. To be able to vary and measure the vertical distance between the concentration sensor and the phase-boundary of the sample.

These requirements were met with varying degrees of success by a sample chamber of quite complex design mounted in a standard He^3 refrigerator cryostat. We decided to measure the concentration by the capacitative technique developed by Heybey

in 1962³⁴ employing a Tunnel Diode Oscillator (TDO). In this way we hoped to achieve the required sensitivity with a relatively simple design. To meet requirement #8, a single parallel plate capacitor was used as the concentration-sensing element. The capacitor plates had to be horizontal and as closely spaced as possible.

Requirement #9 necessitated the most elaborate design. The capacitor measuring sample concentration had to remain stationary for greatest stability; therefore we contrived to move the phase boundary instead, by installing a movable plunger inside the sample chamber. By moving this plunger up and down, the location of the phase boundary could be vertically shifted relative to the location of the capacitor, as shown in Fig. 10.

We monitored temperatures by using semiconductor resistance thermometry, measuring these resistances with AC bridge networks. Temperatures were controlled by allowing a suitable bridge output to drive a current source that heated resistance wires surrounding the sample chamber.

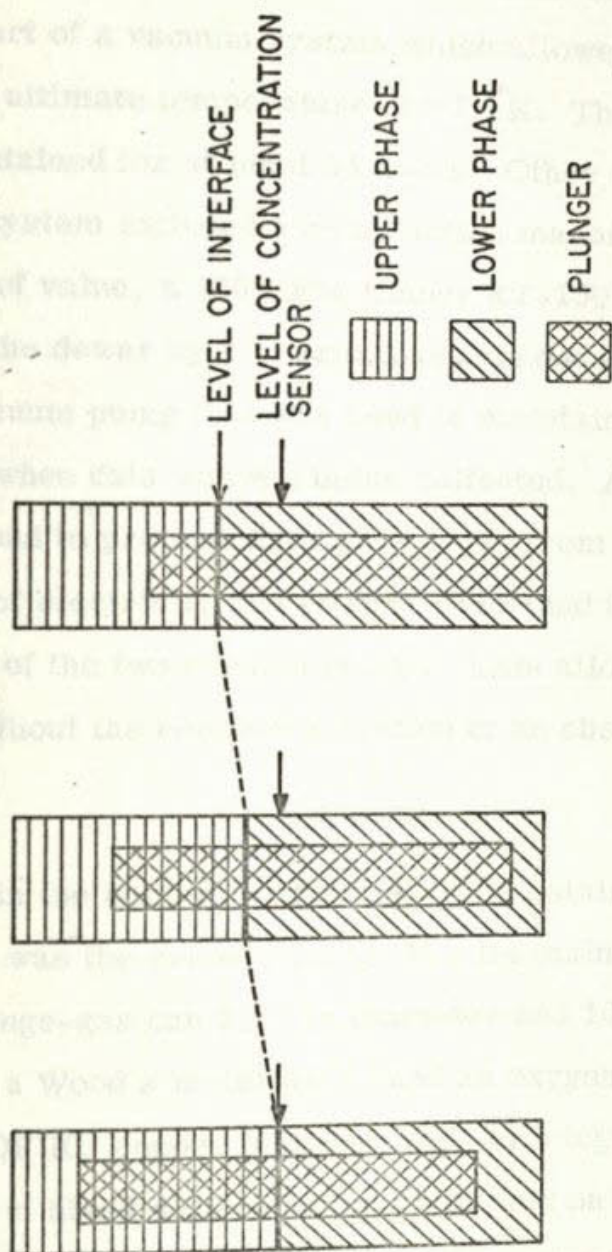
The design of each subsystem of the apparatus is detailed in the following sections.

B. Cryogenics

Low temperatures were maintained by two nested dewars of silvered glass manufactured by Kontes/Martin. The outer dewar of 5.5" I.D. was filled with liquid nitrogen while the inner dewar

Figure 10

An illustration of how plunger motion can affect the relative positions of the interface and the concentration sensor.



of 3" I.D. contained a liquid helium bath. This inner dewar was an integral part of a vacuum system which allowed the bath to be pumped to an ultimate temperature of ~ 1.1 K. This temperature could be maintained for at least 24 hours. Other components of this vacuum system included a combination manometer-over-pressure relief valve, a 150 CFM Kinney KT-150 vacuum pump connected to the dewar by 4" pyrex lines, and a 5 CFM Directorr 8805 vacuum pump that was used to maintain the bath at 2 K and higher when data was not being collected. A fail safe system was devised to protect the Kinney pump from interruptions in the supply of electricity and cooling water and the dewars from failures of the two vacuum pumps. This allowed data runs to continue without the constant attention of an observer.

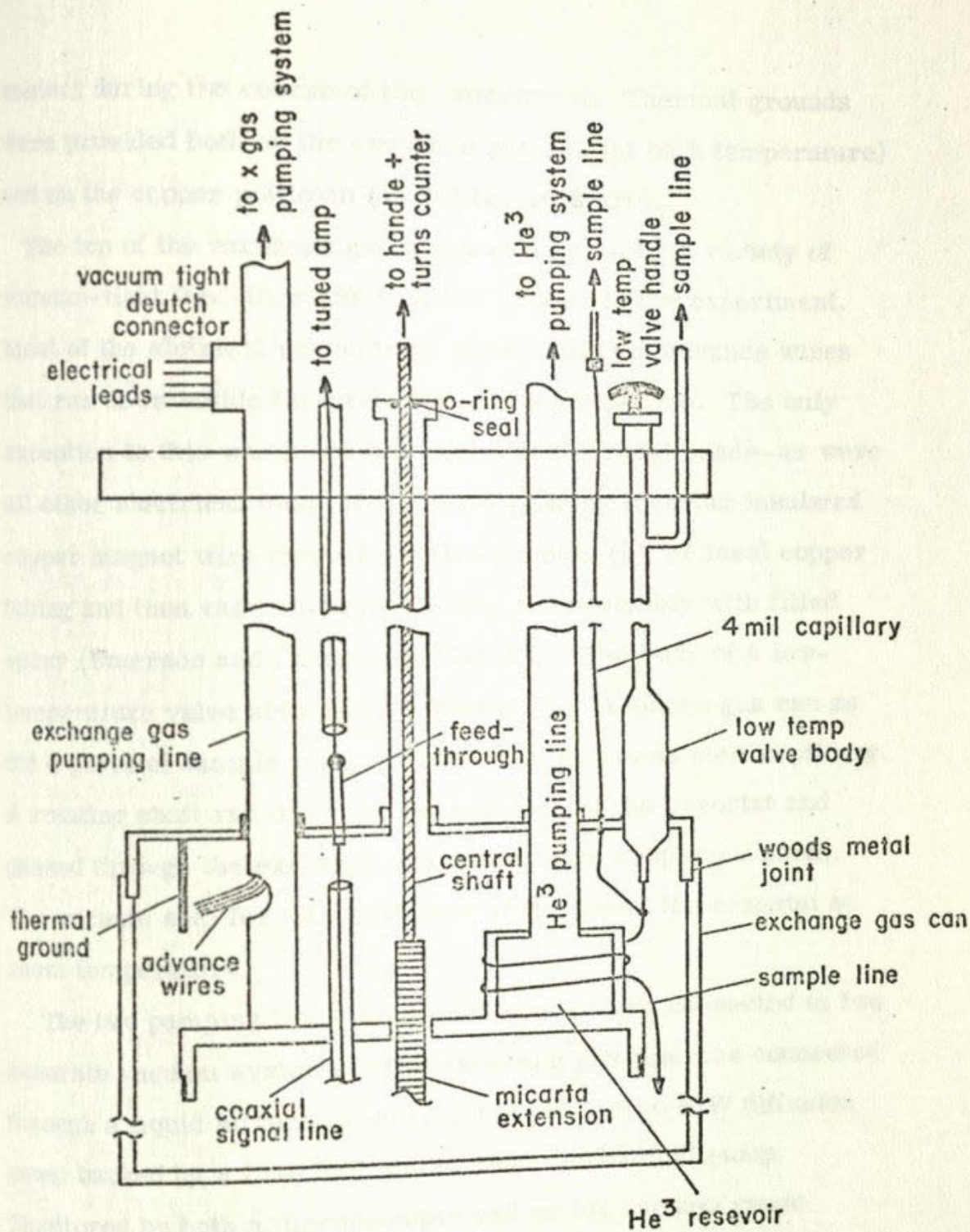
C. Cryostat

Suspended in the helium bath by two T-304 stainless steel pumping lines was the cryostat, Fig. 11. Its main components were an exchange-gas can 2.5" in diameter and 10" long, demountable via a Wood's metal joint, and an oxygen-free high conductivity (OFHC) copper platform with an integrally machined He^3 reservoir of about 4 cc capacity. Pumping on the He^3 in this reservoir permitted the maintenance of the copper platform and any attached equipment in the range from 1 K to 500 mK for periods up to 24 hours. The sample chamber described below was attached to this platform with varying degrees of thermal

Figure 11

The Cryostat

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contact during the course of the experiment. Thermal grounds were provided both on the exchange gas can (at bath temperature) and on the copper platform (at He^3 temperature).

The top of the exchange gas can was pierced by a variety of vacuum-tight feed-throughs to allow access to the experiment. Most of the electrical connections were made via advance wires that ran down inside the exchange gas pumping line. The only exception to this was a coaxial cable feed-through made—as were all other electrical feed throughs—by passing formvar insulated copper magnet wire through small diameter ($\frac{1}{8}$ " or less) copper tubing and then vacuum-impregnating the assembly with filled epoxy (Emerson and Cummings 2860 FT). The body of a low-temperature valve also passed through the exchange gas can as did a parallel sample lines of .004" I.D. stainless steel capillary. A rotating shaft ran down the central axis of the cryostat and passed through the exchange gas can and the copper platform. The vacuum seal for this shaft was at the top of the cryostat at room temperature.

The two pumping lines mentioned above were connected to two separate vacuum systems. The exchange gas line was connected through a liquid nitrogen cold trap to a 4" Veeco 41W diffusion pump backed by a Duo-Seal Model 1400 mechanical pump. Monitored by both a thermocouple and an ion vacuum gauge this system commonly achieved vacuums of 5×10^{-6} Torr in the exchange gas can. The He^3 system was quite similar except that

the exhaust of the mechanical pump - an especially sealed duo-seal model 1402 - was collected in two 1.5l metal storage vessels for re-condensation into the He^3 reservoir. This system also incorporated a Hoke 2331 needle valve between the diffusion pump (which was actually never used) and the He^3 reservoir. By means of this valve the rate of evaporation of He^3 could be controlled to give cooling rates in the neighborhood of 1 mK/Hr in the required temperature range.

D. Sample Chamber

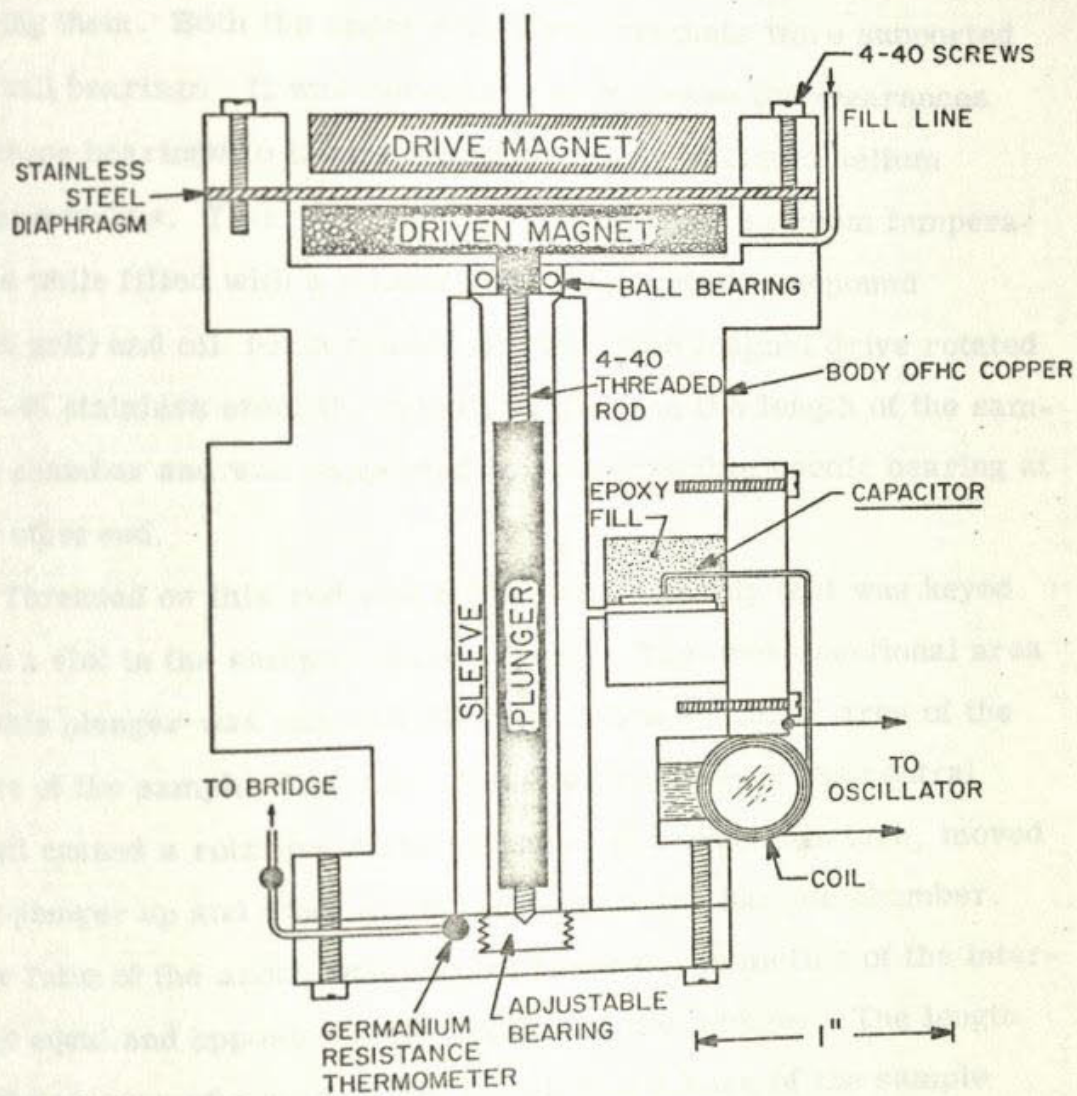
The sample chamber, Fig. 12, was mounted on the copper platform by a threaded brass ring. Thermal contact between platform and chamber was provided by several adjustable copper straps. All electrical leads were first thermally grounded at the bath temperature and then to the He^3 reservoir before entering the sample chamber. The central shaft, of 1/16" stainless steel, was extended by 4" of $\frac{1}{4}$ " Micarta shafting before being attached to the sample chamber. These steps were taken to reduce the heat input to the sample chamber by these routes to a minimum, thus reducing the possibility of thermal gradients.

The body of the sample chamber was machined from a 2.25" diameter cylinder of OFHC copper. The top section of the sample chamber contained the magnet drive, whereby the rotary motion of the central shaft was transmitted inside the sample chamber. The relatively large diameter of the chamber was a constraint imposed by the diameter of reasonably strong magnets.

Figure 12

A cross sectional view of the sample chamber

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SCHEMATIC DIAGRAM OF
SAMPLE CHAMBER

The magnets employed - alnico disks of 1.63" diameter and .26" thickness - were capable of transmitting a torque of several inch-ounces across the 1/16" stainless steel diaphragm separating them. Both the upper and lower magnets were supported by ball bearings. It was necessary to increase the clearances of these bearings to insure smooth running at liquid helium temperatures. This was done by running them at room temperature while filled with a mixture of fine grinding compound (600 grit) and oil for a minute or two. The magnet drive rotated a 4-40 stainless steel threaded rod that ran the length of the sample chamber and was supported by an adjustable needle bearing at the other end.

Threaded on this rod was a plunger assembly that was keyed into a slot in the sample chamber wall. The cross sectional area of this plunger was one half the free cross sectional area of the bore of the sample chamber. Thus the rotation of the central shaft caused a rotation of the threaded rod which, in turn, moved the plunger up and down along the bore of the sample chamber. The ratio of the areas was chosen to make the motion of the interface equal and opposite to the motion of the plunger. The length of the plunger was made $\frac{3}{4}$ the length of the bore of the sample chamber to maximize the distance through which the interface could be moved. The maximum travel of the plunger was $\frac{1}{2}$ " i.e. 20 turns of the drive screw.

The capacitor sub-assembly, used for making dielectric measurements on the sample, was designed to contain sample over as small a vertical height as possible, while attempting to keep stray capacitance to a minimum. It was manufactured by fastening the upper capacitor plate, with its attached electrical connection, into its proper position on the base plate (maintained by a 0.002" plastic shim) with sealing wax. The "epoxy fill" (Emmerson and Cummings 2850 FT) was then added while the entire assembly was enclosed in an appropriately shaped mold coated with a release compound. Warming the capacitor assembly after the epoxy had set allowed removal of the shim, and acetone removed the last traces of sealing wax. This process resulted in a parallel plate capacitor of $\sim 0.004''$ spacing and with a fill factor (the ratio of active to stray capacitance) of better than $\frac{1}{2}$. The capacitor sub-assembly was then mounted in a recess that communicated with the bore of the sample chamber. This design was chosen to minimize pressure effects on the capacitor. Once connected in parallel with a toroidal coil of tinned copper wire wound on a Micarta form, the capacitor became part of a tank circuit with a resonant frequency of ~ 11.5 MHz.

A removable bottom plate on the sample chamber gave access to the bore and plunger area, and contained a germanium resistor (in a He^3 -filled capsule) and its associated electrical feed-throughs as a temperature sensor. All the various sections of the sample chamber were assembled with 0.005" lead O-rings

and brass 4-40 fillister-head screws to create an hermetically sealed unit with an interior sample volume of about 3 cc.

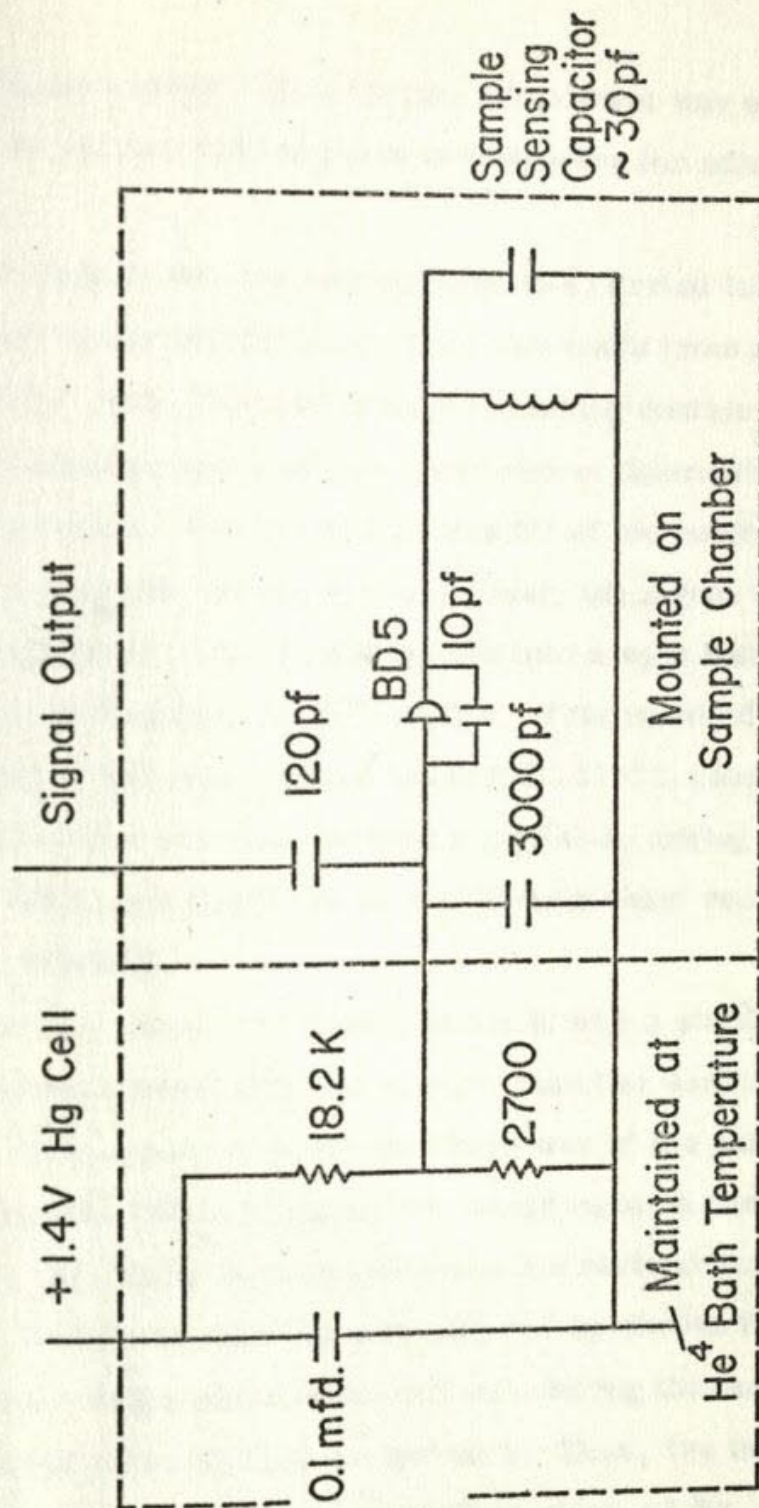
E. Electrical

The tank circuit mentioned above was part of a tunnel diode oscillator (TDO), Fig. 13. The circuit elements of the oscillator were divided into two sections, the biasing resistors being mounted on the exchange gas can heat sink, as they were the main dissipators of heat ($100 \mu\text{W}$), and the diode and associated passive elements being mounted directly on the sample chamber. In order to keep the heat input to the sample chamber as small as possible, the diode was attached to the tank circuit by ~ 1 cm of #39 advance wire, while it was connected to its voltage supply by four strands of #18 copper wire thermally anchored to the He^3 pot. It was thus our hope that the majority of the $\sim 2 \mu\text{W}$ dissipated in the tunnel diode would not enter the sample chamber at all.

The TDO was powered by a 1.35 V "D" size mercury battery. In order to minimize temperature effects upon this cell it was mounted on a 500 g aluminum block and surrounded by one inch styrofoam walls to create a long thermal time constant. This was necessary because the TDO frequency varies slightly according to the biasing voltage on the diode. The output of this cell could be fed either directly to the biasing resistors of the TDO or through a $25 \text{ K}\Omega$ potentiometer, enabling us to adjust

Figure 13

Schematic diagram of the Tunnel Diode Oscillator



Tank Coil 84t. #24
tinned Cu on toroidal
Micarta form

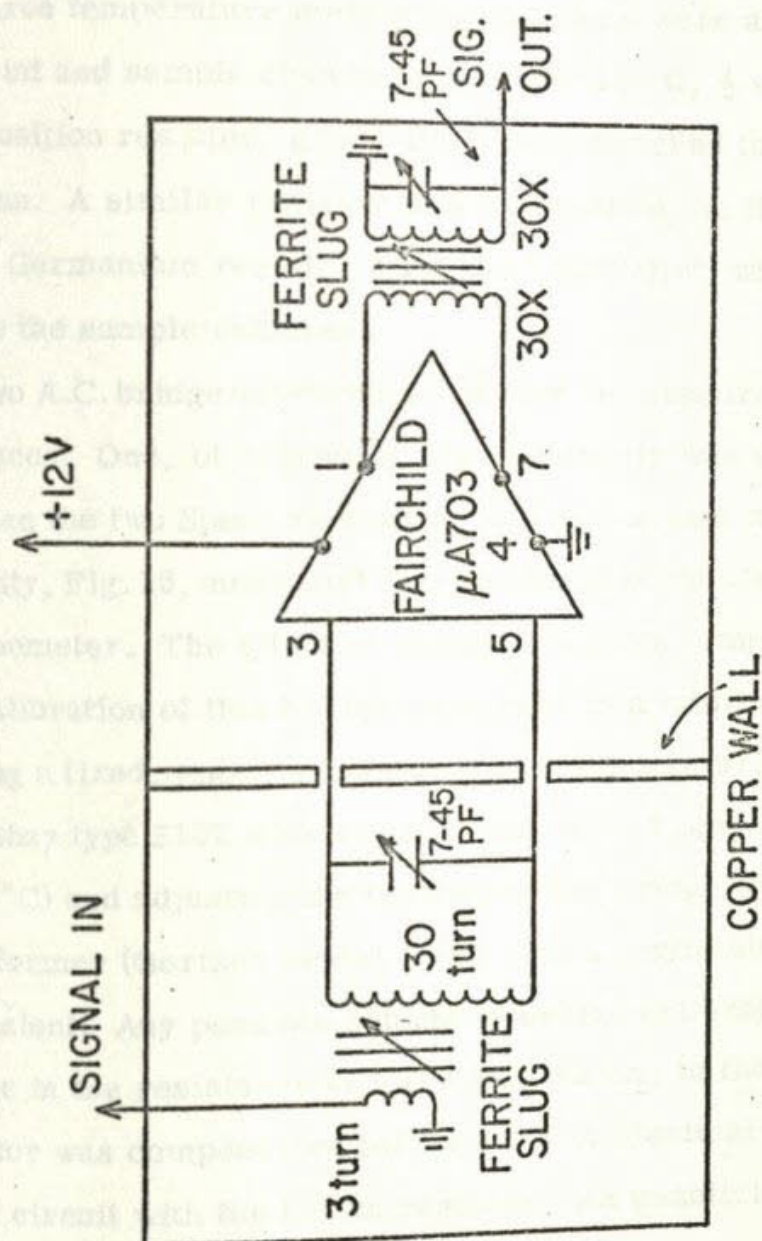
the biasing voltage. This biasing adjustment was necessary only when we ran the TDO at room temperature for adjustment purposes.

The signal from the tunnel diode was carried to the top of the cryostat by the coaxial line. This was made from a piece of $\frac{1}{8}$ " O.D. 0.01" wall, 304 stainless steel tubing containing a teflon tubing insulator and a center conductor of alternating copper and advance wires. The top and bottom 6" of the center conductor were of advance. At the cryostat head, the signal was fed into a tuned amplifier, Fig. 14 and thence into a wide band amplifier - an Hewlett Packard, (H.P.), 8447 A. This resulted in a 0.3 V rms signal that was counted by an H.P. 5245 L counter. The counter output was then fed into a digital-to analog converter (H.P. 580 A) and displayed on a 10" strip chart recorder (H.P. 7100 BM).

The TDO ran at ~ 11.5 MHz at 1.1 K with a stability of ± 0.5 Hz over several hours with the sample chamber empty. The dependence of frequency upon temperature was of the same order - 0.12 Hz/mK. Since a typical run would cover a range of about 10 mK, this would lead to frequency corrections on the order of 1 Hz. Long term stability was affected by sudden frequency jumps of ~ 30 Hz which occurred only during the thermal cycling associated with refilling the He⁴ bath. Thus, the intrinsic stability of the TDO during a run was about ± 1 Hz, not including the effects of actual concentration instabilities in the sample.

Figure 14

Schematic diagram of the tuned amplifier



TUNED AMPLIFIER

Between runs, frequency changes of ~ 30 Hz were possible.

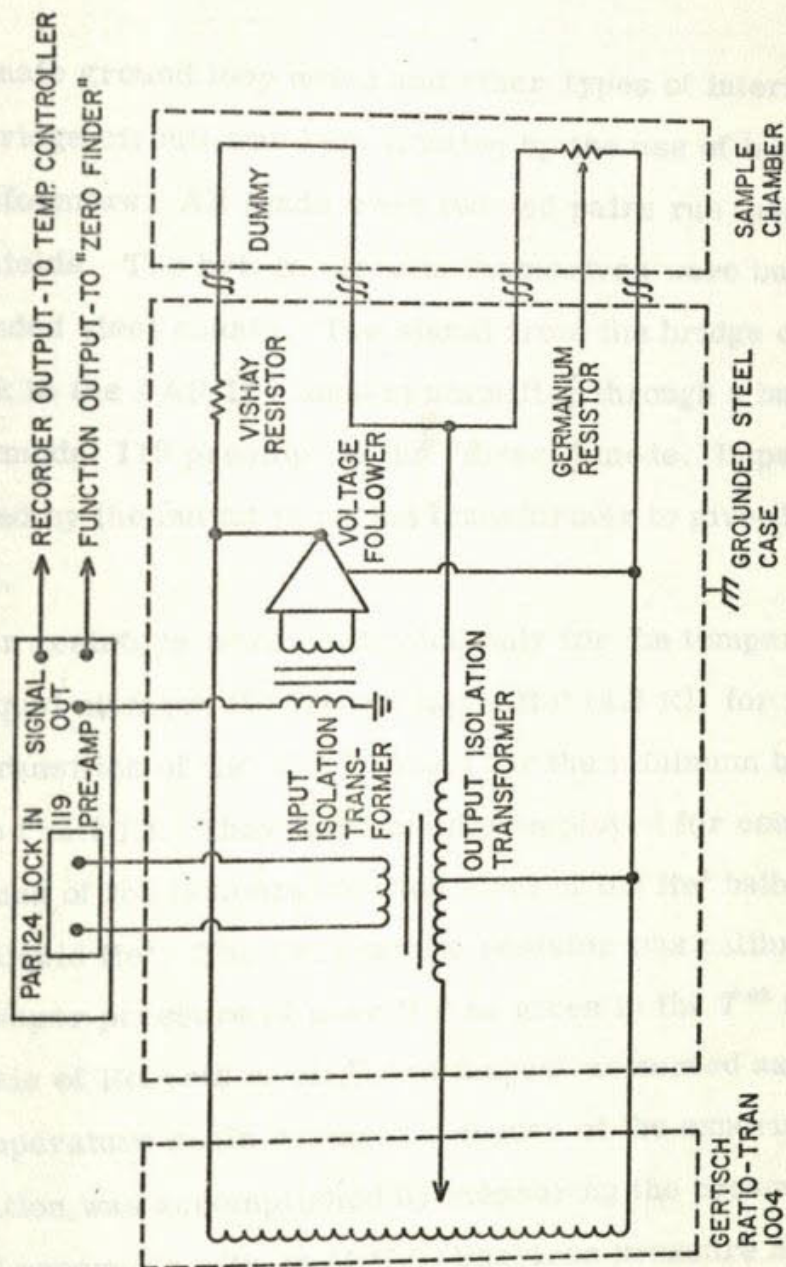
F. Temperature Measurement

Three temperature measuring elements were attached to the cryostat and sample chamber. A Speer $100\ \Omega$, $\frac{1}{2}$ watt carbon composition resistor, grade 1002, was attached to the exchange gas can. A similar resistor was mounted on the He^3 reservoir, and a Germanium resistor (Cryocal CR500- He^3) was mounted inside the sample chamber.

Two A.C. bridge networks were used to measure these resistances. One, of relatively low sensitivity was switchable between the two Speer resistors, and one of high sensitivity and stability, Fig. 15, measured the resistance of the Germanium thermometer. The effect of changes in room temperature upon the calibration of this bridge were kept to a minimum by employing a fixed, known resistor of low temperature coefficient (a Vishay type S102 with a coefficient of 0 ± 1 ppm/ $^\circ\text{C}$ between $0 - 60^\circ\text{C}$) and adjusting the balance of the bridge with a ratio transformer (Gertsch model 1004) with a negligible temperature coefficient. Any possible change of bridge calibration due to a change in the resistance of the wires leading to the Germanium resistor was compensated for by a set of identical leads included in the circuit with the known resistor. An unanticipated benefit of this sort of circuit is that readings given by the ratio transformer were approximately linear in temperature over a very

Figure 15

Schematic diagram of the A.C. resistance bridge circuit



wide range (600 - 900 mK), even though the resistance of the Germanium thermometer changes exponentially with temperature.

To eliminate ground loop noise and other types of interference, the entire bridge circuit was kept floating by the use of input and output transformers. All leads were twisted pairs run inside grounded shields. The bridge circuits themselves were built inside a grounded steel chassis. The signal from the bridge circuit was fed back to the PAR 124 lock-in amplifier through a balanced input to the model 119 preamp. in the "direct" mode. Impedances were matched by the output isolation transformer to give the best noise figure.

The Speer resistors were calibrated only for the temperatures of boiling liquid nitrogen (77 K) and liquid He⁴ (4.2 K), for the superfluid transition of He⁴ (2.17 K) and for the minimum bath temperature (~1.1 K). They were mainly employed for coarse determinations of the temperature and level of the He⁴ bath during transfer of liquid He⁴. The Germanium resistor was calibrated against the vapor pressure of pure He³ as given in the T^{62} temperature scale of Roberts *et al.*,³⁵ and thereafter served as the primary temperature scale during the course of the experiment. This calibration was accomplished by measuring the pressure over the He³ reservoir with an M.K.S. Barytron pressure meter, type 1200, equipped with a model 145 AH head capable of measuring 10 mm Hg full scale with an absolute accuracy of a part

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in 10^4 . The Barytron itself was calibrated both against an oil manometer and a dead-weight pressure gauge manufactured by the Ruska Instrument Corporation, whose accuracy is traceable to the National Bureau of Standards.

The Barytron, besides giving a most accurate and convenient method of measuring the He^3 vapor pressure, allowed us to constantly observe and record this pressure on the strip chart record of the experiment, thus guarding against changes in the calibration of the Germanium resistor and associated circuitry.

Temperature calibrations were carried out in both slowly warming and cooling modes at rates not exceeding 4 mK/Hr. These results were averaged to compensate for any temperature differential between the sample chamber and the He^3 reservoir. The sensitivity of the bridge allowed relative temperature measurements of 4 μK and the calibration procedure resulted in an accuracy of $\pm .3$ mK relative to the T^{62} scale.

The final element of the temperature measuring system was the "zero finder". This was simply an operational amplifier driven by the function output of the PAR 124. Because of the extremely large amplification factor of the operational amplifier, its output would essentially always be driven to one of its extremes, ± 10 V, except when the input signal passed through zero, at which point the amplifier output would jump from one extreme to the other. This output voltage was channeled by diodes to operate a relay when the amplifier output went negative.

The relay had both normally-open and normally-closed contacts which were used to energize the event marker on the strip chart recorder, and a buzzer warning the experimentalist that the desired temperature had been reached.

G. Temperature Control

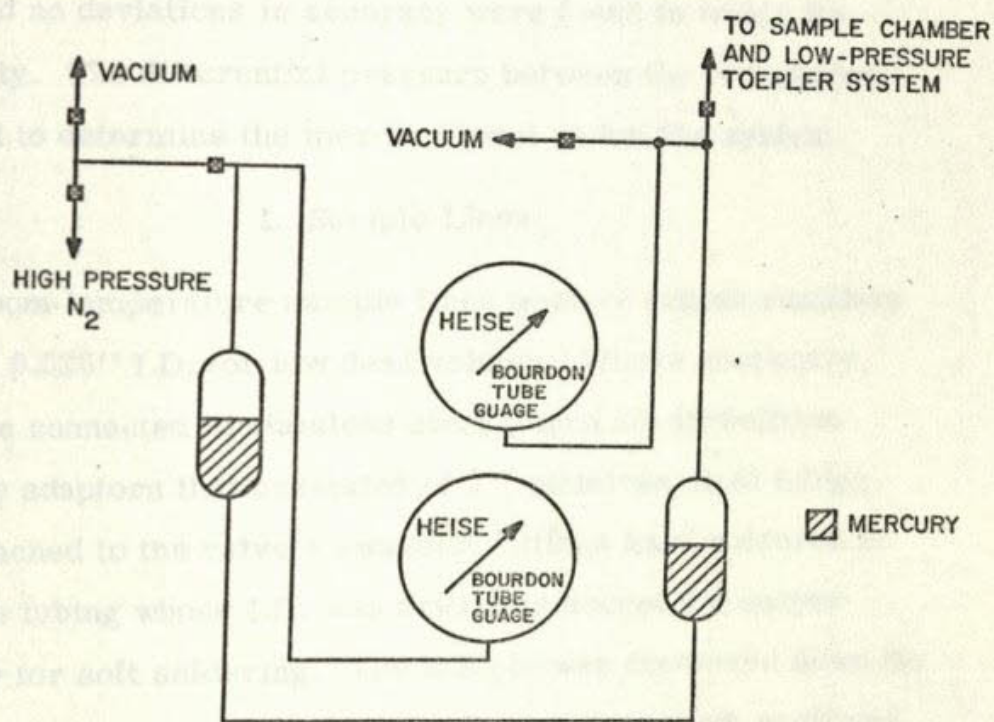
Temperature control was accomplished by allowing the output of the PAR 124 to control a current source, whose output could be divided among any of four heaters inside the cryostat. All heaters were wound of #39 advance wire, one on the He³ reservoir and three at various levels on the sample chamber. By thus distributing the heat input to the sample, we hoped to minimize the effect of any thermal gradients thus induced. This system, when driven by the bridge at a PAR 124 sensitivity of 2 μ V with a 3 second time constant could maintain temperatures to within 20 μ K. A manual heating feature allowed coarse temperature adjustments to be made by hand.

H. Pressure Measurement and Control

Pressures were both maintained and measured by a high pressure gas handling system, Fig. 16. Built entirely of stainless steel, the system used Nupro SS-4H bellows valves connected to $\frac{1}{8}$ " tubing of 0.030" wall by Swagelok joints. The reservoirs were 1 liter high pressure sample cylinders, rated at 1500 pSIG, with $\frac{1}{2}$ " NPT connectors at each end.

Figure 16

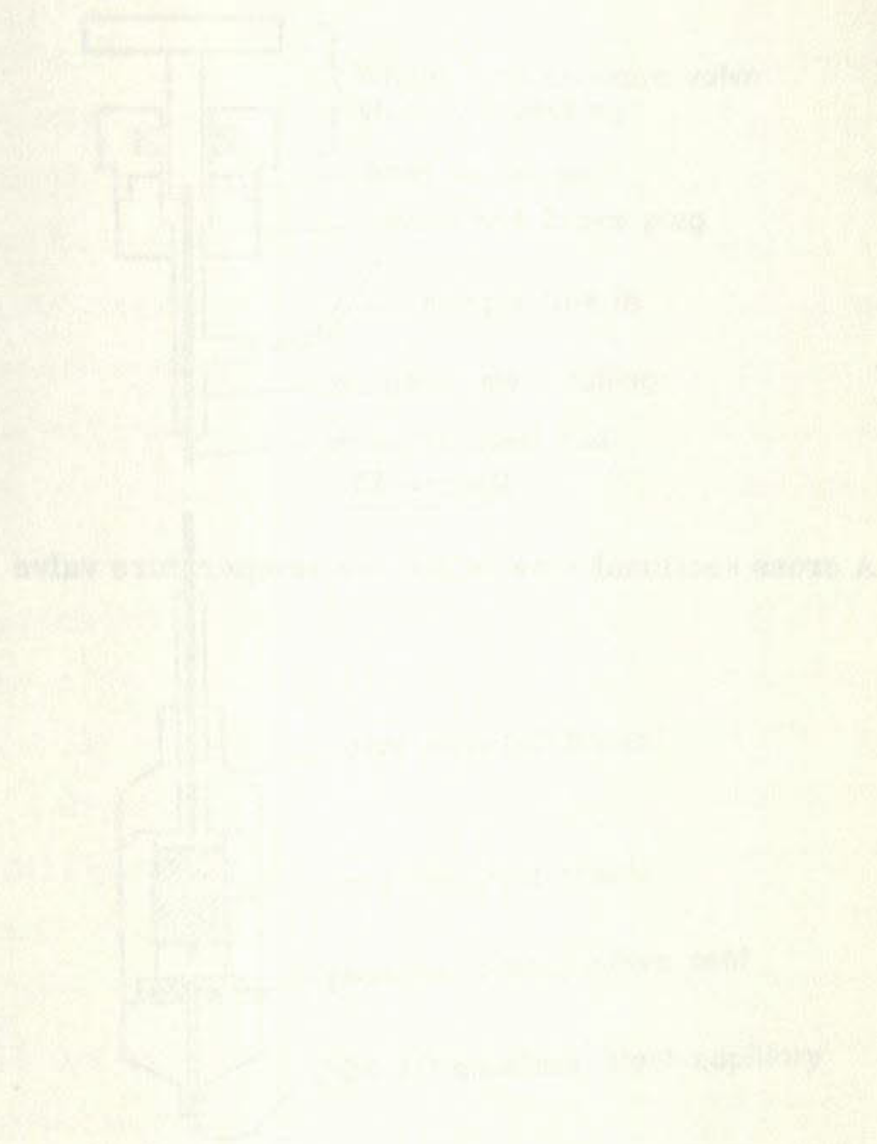
Schematic diagram of the high pressure gas handling system



The system used nitrogen gas to force a mercury "piston" to compress the sample to the desired pressure. Heise Bourdon tube gauges model C 58150 with a range of 0 - 30 atmospheres and a sensitivity of 0.01 atm. were used to measure the pressure on either side of the mercury. The gauge that measured sample pressure was calibrated against the above mentioned dead weight gauge and no deviations in accuracy were found to within its sensitivity. The differential pressure between the two gauges was used to determine the mercury level within the system.

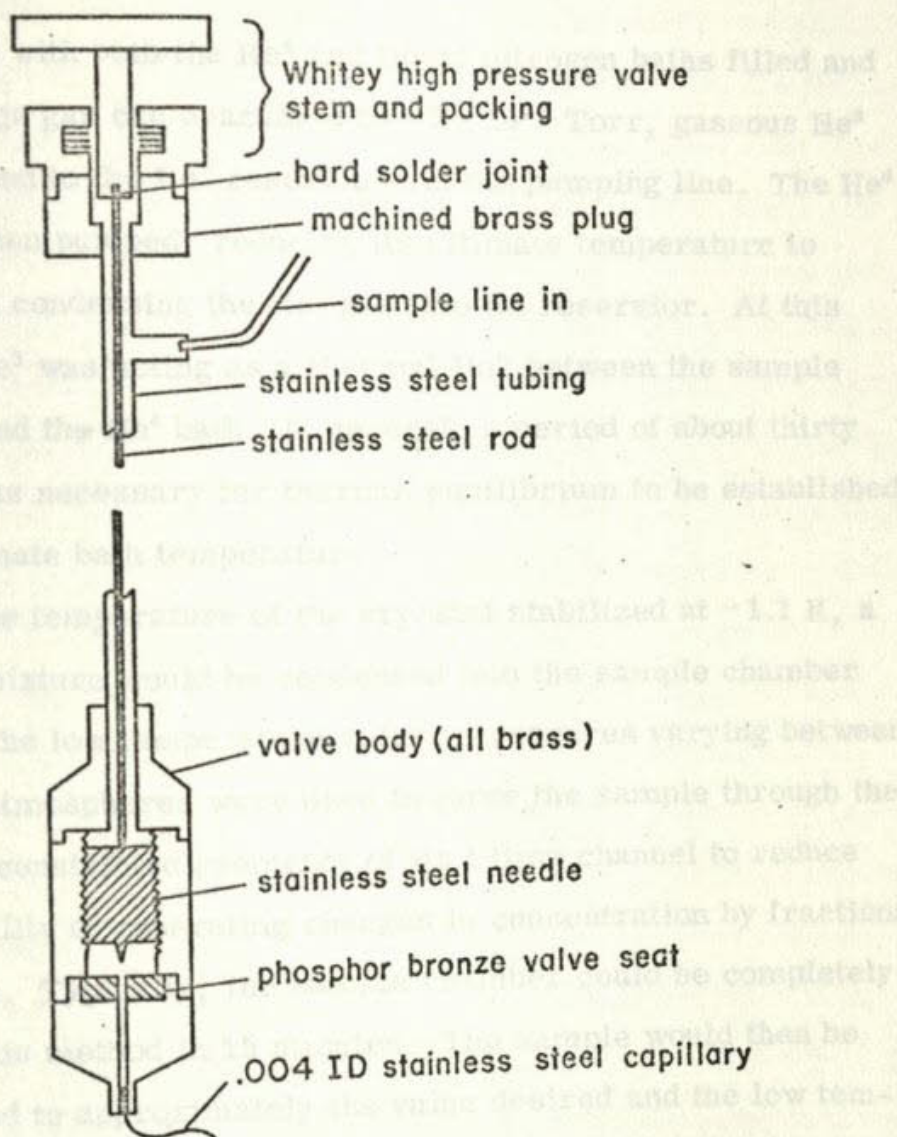
I. Sample Lines

All room temperature sample lines were of copper capillary tubing of 0.026" I.D. for low dead volume. Where necessary, they were connected to stainless steel Nupro SS-4H bellows valves by adaptors that consisted of $\frac{1}{8}$ " stainless steel tubing to be attached to the valve's Swagelok fittings hard soldered to $\frac{1}{8}$ " brass tubing whose I.D. was drilled to accept the copper capillary for soft soldering. The sample was conducted down the cryostat via two routes: a 0.004" I.D. stainless steel capillary valved at room temperature, and a low temperature valve, Fig. 17, whose valve stem was the sample channel. Once the low temperature valve was closed, the sample chamber and associated 4 mil capillaries were isolated from the rest of the system, thus maintaining the concentration integrity of the sample.



V. Procedure and Results

A. A Typical run



V. Procedure and Results

A. A typical run

Starting with both the He^4 and liquid nitrogen baths filled and the exchange gas can evacuated to $\sim 5 \times 10^{-6}$ Torr, gaseous He^3 was admitted to the He^3 reservoir via the pumping line. The He^4 bath was then pumped, reducing its ultimate temperature to ~ 1.1 K and condensing the He^3 gas into its reservoir. At this time the He^3 was acting as a thermal link between the sample chamber and the He^4 bath. In general, a period of about thirty minutes was necessary for thermal equilibrium to be established at the ultimate bath temperature.

When the temperature of the cryostat stabilized at ~ 1.1 K, a He^3 - He^4 mixture would be condensed into the sample chamber by way of the low temperature valve. Pressures varying between 1.5 and 6 atmospheres were used to force the sample through the somewhat constricted geometry of its filling channel to reduce the possibility of generating changes in concentration by fractional distillation. Typically, the sample chamber could be completely filled by this method in 15 minutes. The sample would then be pressurized to approximately the value desired and the low temperature valve closed. The top of the valve stem would then be isolated from the rest of the high-pressure system so that any subsequent fractional distillation of the sample within the valve

stem could not affect the concentration of the remaining room temperature mixture.

The filling of the sample chamber, initially under vacuum, was graphically portrayed by the frequency readout on the strip chart recorder. As soon as the sample began to enter, the frequency would drop by about 3 KHz, indicating that the dielectric constant between the capacitor plates had been increased by the presence of gas and, perhaps, superfluid film. The frequency would then remain constant to within a few hundred Hz until the liquid level reached the height of the capacitor. The filling of the capacitor with liquid would cause a precipitous drop in frequency (150 KHz in 2 minutes). The frequency would then stabilize again. The completion of the filling operation would be marked by another sudden downward excursion in frequency as the sample became pressurized. This pressurization would be continued until an appropriate pressure range was reached. When the frequency finally stabilized again, it was concluded that no pressure gradients remained in the system and that the pressure read at the high pressure gas handling system accurately reflected the pressure inside the sample chamber. The closing of the low temperature valve would induce small frequency changes on the order of 20 Hz indicative of changes either in pressure (~ 0.03 Atm) or, less likely, concentration induced by this action.

The sample chamber would then be cooled by pumping on the He^3 reservoir until a temperature of 870 mK was reached. This

temperature would be maintained by the temperature controller. The pressure was then trimmed by opening the valve on the 4 mil capillary until a stable frequency again indicated pressure equilibrium. In general, the pressure of the sample would increase by about 0.3 atm. during this cool-down. The 870 mK temperature was chosen as appropriate for trimming the pressure as the sample could have no superfluid component at this temperature over the range of pressures and concentrations considered. It was feared that initiating a flow of sample while some of it was superfluid would result in a "heat flush" effect that might drastically alter the concentration. After again isolating the sample chamber from the high pressure gas handling system, it would be cooled to the range of temperature in which we anticipated that phase separation would take place.

Our first aim was to determine the concentration of the sample relative to the tricritical concentration ($X - X_c$) at the pressure being studied. This was done by cooling the sample through the phase separation temperature twice, once with the plunger in its bottom position and once with the plunger at the top. If $X \ll X_c$ the onset of phase separation would be marked by a drop in oscillator frequency during both cooling runs. The drop in frequency was due to the increase in He^4 concentration of the lower phase. That both cooling runs showed similar drops in frequency was indicative of a phase boundary coming into existence above the scanning range of the sample chamber.

Analogously if $X \gg X_c$ the onset of phase separation would be marked by an increase in frequency during both cooling runs.

Once the concentration of the sample relative to X_c was determined, we would adjust the value of $X - X_c$ by changing the pressure of the sample by way of the 4 mil line. This would change X_c while, hopefully, leaving X constant. Our goal in this procedure was to finally arrive at a value of $X - X_c$ for which the two cooling runs described above would show opposite frequency effects, indicating that the phase boundary had formed within the scanning range of the sample chamber. Several cooling runs would then be done with the plunger in various positions in the sample chamber. Usually some small additional corrections to the pressure were necessary to cause the point of formation and subsequent motion of the interface with decreasing temperature to be appropriate for the taking of data. We would strive for a value of $X - X_c$ that would form the interface relatively high in the sample chamber at $T = T_c$ and keep its motion to a minimum for temperatures slightly less than T_c . In the case depicted in Fig. 9, for example, we would attempt to achieve a relative concentration of -0.001 .

We had originally hoped that when the correct pressure had been achieved, it would be possible to take data by simply holding temperature constant and varying the plunger position, thus directly measuring the variation in concentration with the distance from the interface. Unfortunately, the heating and vibration

associated with the rotation of the magnet drive were sufficient to induce permanent shifts of up to 30 Hz in the oscillator output. Since the effect for which we are searching has a breadth on the order of 100 Hz, it was clearly impossible to take data in this fashion. We therefore elected to take data by varying temperature while keeping the plunger position constant. We would begin at some temperature sufficiently high to guarantee that the gravitational effects were negligible and cool slowly at rates less than 4 mK/Hr. until a point about 10 mK below the phase separation temperature was reached. The sample would then be warmed, the plunger moved to a new position, and the process repeated. This procedure allowed us to compensate for the frequency changes caused by the use of the magnet drive by adjusting our data so that the concentration measured at the highest temperature during the run, assumed equal to the average concentration of the sample, was always the same. To further guarantee that these adjustments were accurate, the concentrations measured by the capacitor below the temperature range in which gravitational effects were important also had to agree for the data to be considered valid. Then data taken at the same temperature from runs at different plunger positions could be correlated to explore the relationship between the desired variables.

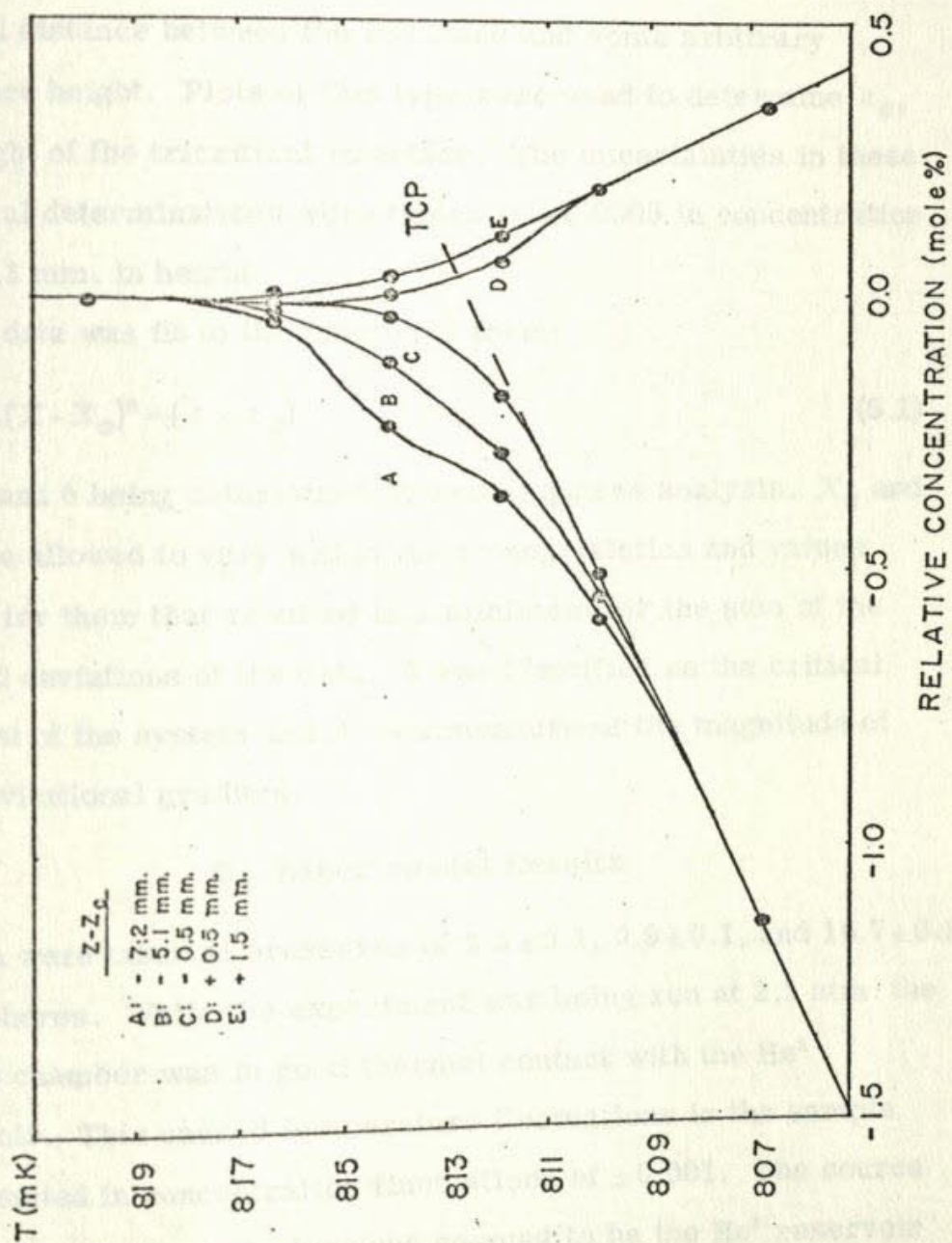
B. Methods of Data Analysis

We have previously described the methods employed in determining the pressure and temperature of the sample. Relative concentrations were measured by determining the concentration sensitivity of our TDO circuit. As is shown in Appendix D there is a linear relationship between changes in frequency and changes in concentration, eq. D-12. The constant of proportionality depends upon what pressure is being considered. The relative motion of the interface caused by movement of the plunger is a bit more complex. We assumed, as a first approximation, that the motions of the plunger and the interface were equal and opposite. This would be rigorously true only if the interface separated two phases of uniform concentration. From this assumption it was possible to determine an initial concentration profile of the sample at various temperatures. This concentration profile was used to calculate interfacial motion curves of the type shown in Fig. 9 for the different internal geometries caused by different plunger positions. From a set of these curves at different plunger positions, the actual motion of the interface caused by changing the plunger position could be determined. The actual motion of the interface was discovered to be approximately linear in plunger position, but deviations in linearity by as much as 3% had a significant effect on the determination of critical exponents.

Fig. 18 shows how typical data at different plunger positions appeared when plotted on $T-X$ coordinates. These plots were

Figure 18

Typical data from cooling runs at different plunger positions plotted on T - X coordinates. The left hand branch of the co-existence curve is extended towards the TCP (dotted line) for the determination of T_c and the relative value of X_c . Only a few data points are shown, for clarity.



also used to determine T_c and X_c by extending the left and right hand branches of the coexistence curve towards the TCP. Fig. 19, shows the same data plotted in $z - X$ space where z is the vertical distance between the interface and some arbitrary reference height. Plots of this type were used to determine z_c , the height of the tricritical interface. The uncertainties in these graphical determinations were typically ± 0.0005 in concentration and ± 0.3 mm. in height.

The data was fit to the functional form:

$$A(X - X_c)^\delta = (z - z_c) \quad (5.1)$$

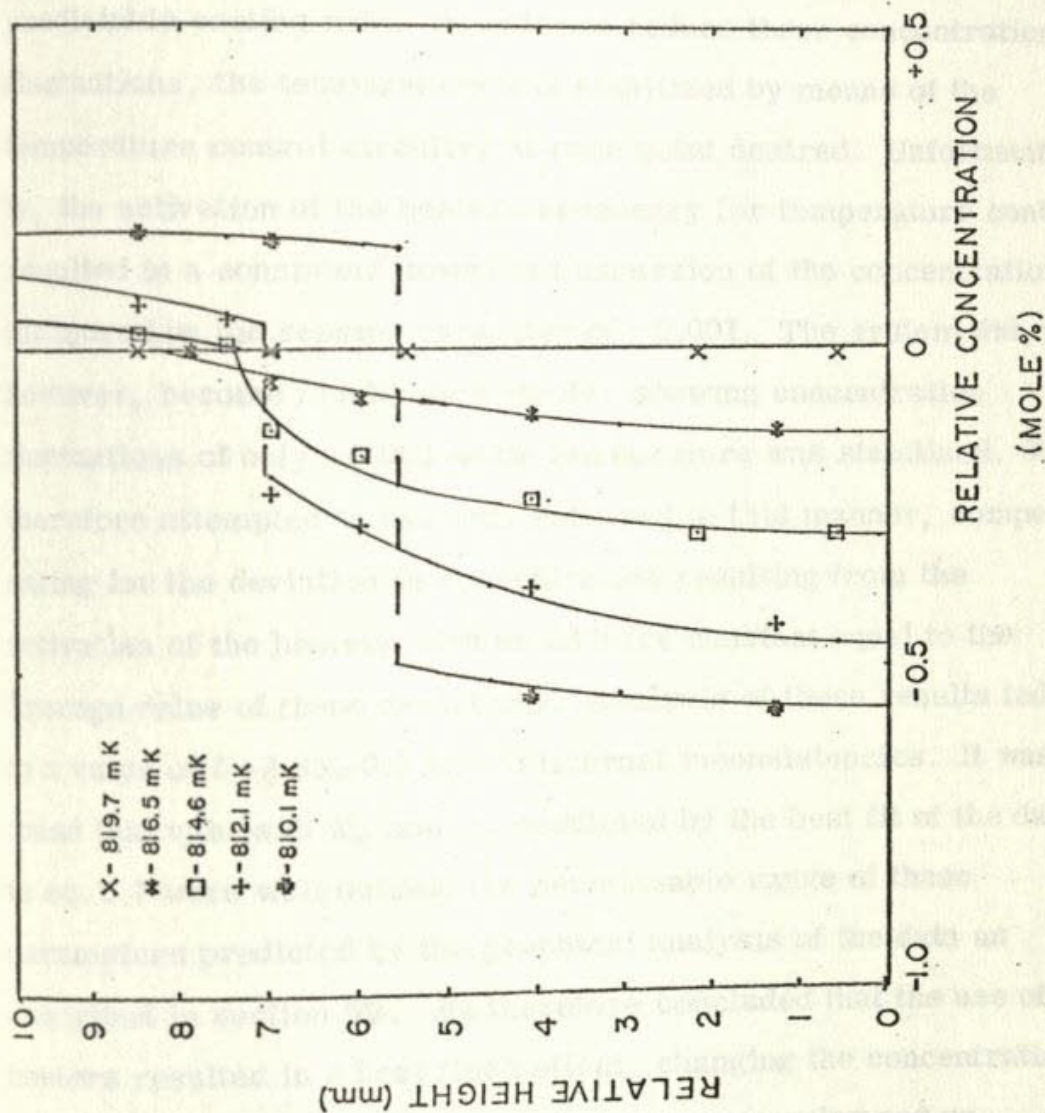
with A and δ being determined by least squares analysis. X_c and z_c were allowed to vary within their uncertainties and values chosen for them that resulted in a minimum for the sum of the squared deviations of the data. δ was identified as the critical exponent of the system and A as a measure of the magnitude of the gravitational gradient.

C. Experimental Results

Data were taken at pressures of 2.5 ± 0.1 , 9.9 ± 0.1 , and 16.7 ± 0.1 atmospheres. While the experiment was being run at 2.5 atm. the sample chamber was in good thermal contact with the He^3 reservoir. This caused temperature fluctuations in the sample that resulted in concentration fluctuations of ± 0.001 . The source of these temperature fluctuations seemed to be the He^3 reservoir

Figure 19

The same data as in Fig 18, plotted on $X - z$ coordinates at different values of T . The height at which the interface disappears determines z_c . Interfaces are shown as dotted lines. Only a few data points are shown, for clarity.



itself. We assume that some defect in the metering valve or, perhaps, a superheating of the liquid He^3 in the reservoir and its subsequent relaxation by way of violent boiling resulted in an unpredictable cooling rate. In order to reduce these concentration fluctuations, the temperature was stabilized by means of the temperature control circuitry at each point desired. Unfortunately, the activation of the heaters necessary for temperature control resulted in a consistent downward excursion of the concentration measured by the sensing capacitor of ~ 0.001 . The system did, however, become much more stable, showing concentration fluctuations of only ± 0.002 while temperature was stabilized. We therefore attempted to use data gathered in this manner, compensating for the deviation in concentration resulting from the activation of the heaters with an additive constant equal to the average value of these deviations. Analysis of these results led to a value of $\delta = 2.85 \pm 0.3$ and to internal inconsistencies. It was found that values of X_c and z_c predicted by the best fit of the data to eq. 5.1 were well outside the permissible range of these parameters predicted by the graphical analysis of the data as described in section 5B. We therefore concluded that the use of heaters resulted in a heat flush effect, changing the concentration being measured by the TDO circuit in some complex and unpredictable way. The results were then reanalyzed, taking concentration values at points where temperature was not being stabilized. The strip chart record was smoothed as best

as possible by eye in order to compensate for the concentration fluctuations. Fortunately, the extrapolated value of T_c was not one of the points where temperature stabilization was employed. As we shall see, this analysis gave results of greater internal consistency and in better agreement with previous work.

The cryostat was modified by reducing the thermal contact between the sample chamber and the He^3 reservoir before the remainder of the data were taken. This resulted in much smoother cooling rates, since the sample chamber would no longer "track" each small excursion of the He^3 reservoir in temperature, but rather respond to its general downward trend. This improved cooling was reflected in levels of concentration stability that were formerly achievable only by the use of heaters. The remainder of the data was therefore taken without employing the heaters at cooling rates of less than 4 mK/Hr.

The sensitivity of our results to heat input to the sample chamber was a cause of some concern. Since the relatively large size of the sample chamber precluded the use of any sort of heat shield, we feared that the heat leak to the sample chamber might adversely affect our results just as had the use of the heaters. In order to investigate this possibility, runs were conducted in both warming and cooling modes, presumably affecting both the magnitude and the pattern of the heat input to the sample chamber. The results were identical to within the accuracy of the experiment. We therefore concluded that our results were not being

influenced by any heat flush effect.

These results are displayed in Fig. 20. The horizontal axis displays the deviation of the concentration from its critical value in mole - %. The vertical axis displays the distance below the tricritical interface in millimeters. The solid curves are plots of eq. 5.1 with the "best fit" values for A , δ , X_c and z_c . The 2.5 atm. data and the 9.9 atm. data are shown in Fig. 20(a), demonstrating the change in gravitationally induced concentration gradient between those two pressures. The 16.7 atm. data are shown in Fig. 20(b) for clarity, as it would otherwise overlay the 2.5 atm. data almost exactly. These results are shown in tabular form below:

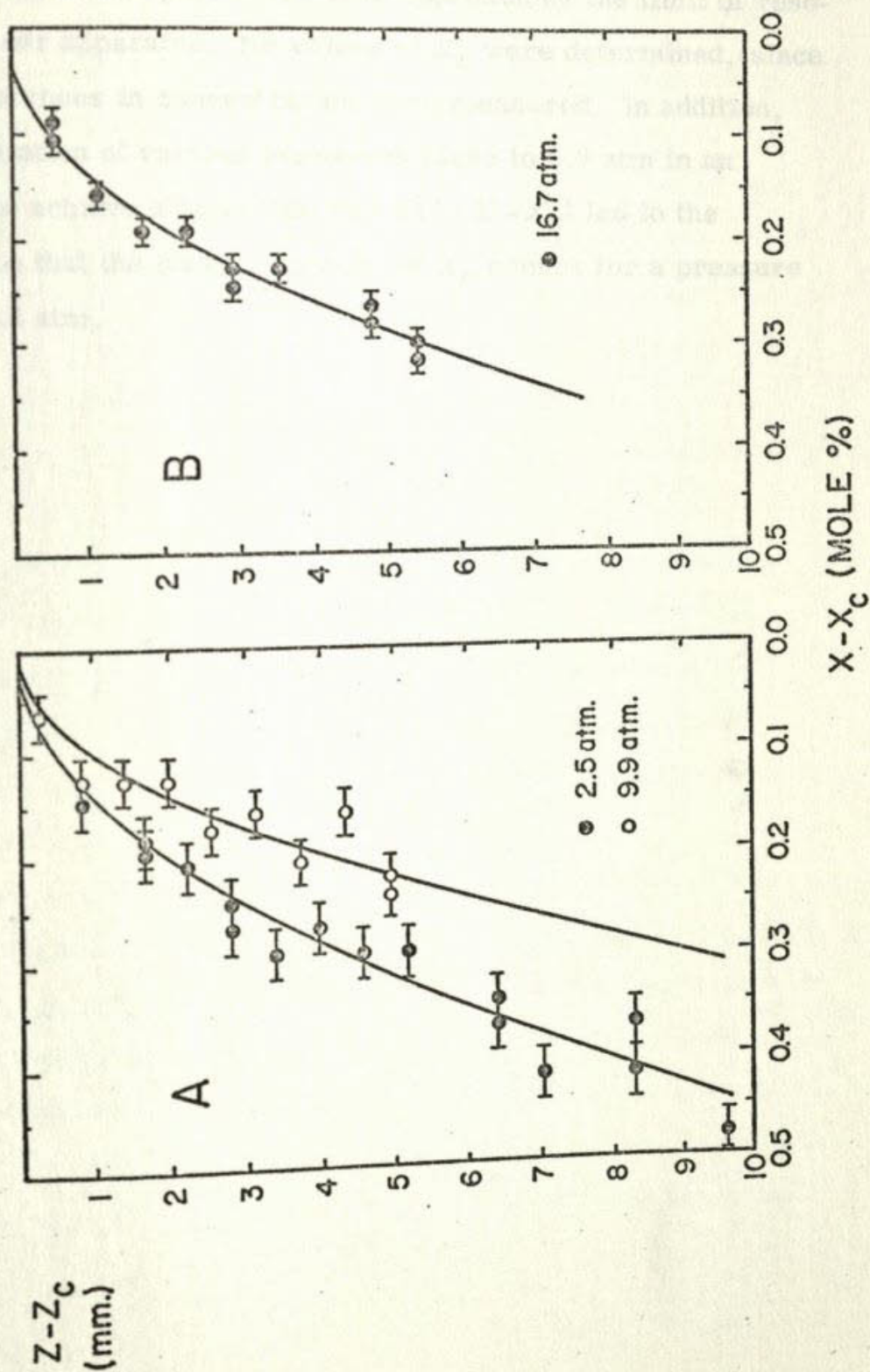
Table 5.1

Pressure(atm.)	T _c (mK)	$A\left(\frac{\text{cm}}{(\text{mole}\%)^2}\right)$	δ	$A_2\left(\frac{\text{cm}}{(\text{mole}\%)^2}\right)$
2.5 ± 0.1	813 ± 0.5	4.7 ± 0.9	1.94 ± 0.2	4.91 ± 0.2
9.9 ± 0.1	759 ± 0.5	7.3 ± 5	1.81 ± 0.48	9.97 ± 0.9
16.7 ± 0.1	740 ± 0.5	6.8 ± 2	2.10 ± 0.2	5.86 ± 0.2

As can be seen, these results are consistent with $\delta = 2$ at all pressures. In all cases values of X_c and z_c that resulted in a best fit to eq. 5.1 were within the limits determined by graphical analysis. Since A is a very strong function of δ , we have also calculated A_2 , the amplitude factor when $\delta \equiv 2$, as a measure of the size of the concentration gradient. The relatively large

Figure 20

- a) Data taken at 2.5 and 9.9 atmospheres plotted on $X-z$ coordinates. Note that the concentration gradient is reduced by nearly a factor of two at the higher pressure.
- b) Data taken at 16.7 atmospheres on the same coordinates. This graph is shown separately for clarity, as it almost exactly overlays the 2.5 atm data.



uncertainties at 9.9 atm. are a result of the reduction in the size of the effect at that pressure. It is approaching the limit of resolution of our apparatus. No values of X_c were determined, since only differences in concentration were measured. In addition, the exploration of various pressures close to 9.9 atm in an attempt to achieve a favorable value of $(X - X_c)$ led to the conclusion that the maximum value of X_c occurs for a pressure of 9.9 ± 0.4 atm.

VI. Conclusions and Summary

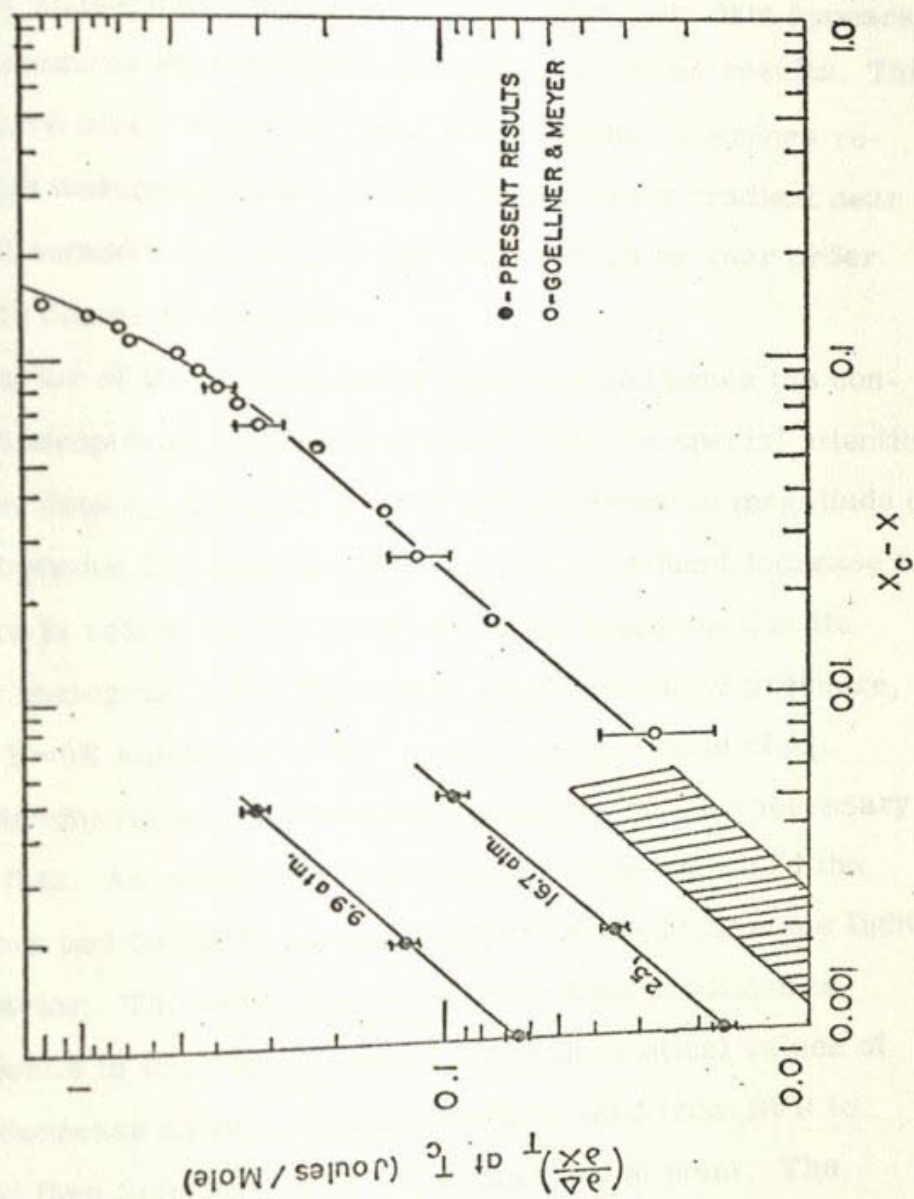
A. Comparison with Theory and Previous Experiment

All of our values of δ are consistent with $\delta \equiv 2$. This is in agreement both with all the theoretical models considered and with the SVP experimental results of Zimmermann¹² *et al.* and Goellner and Meyer.¹³ That the value of δ seems independent of pressure in a system all of whose other parameters vary strongly with pressure is in support of the principle of universality. The magnitudes of our measured concentration gradients are in agreement with the one other measured value, due to Watts¹⁴, at SVP. Again, assuming $\delta \equiv 2$, his data (one point) would lead to a value for A_2 of $1.6 \pm {}^{0.9}_{0.5}$. An extrapolation of our values to $P=0$, although rather uncertain, does not disagree with this value. More importantly, correction routines generated from our results correctly predict the deviations in concentration observed by Rohde¹⁹ and Johnson¹⁸ in their explorations of the behavior of the TCP under pressure.

A much more stringent test of the magnitudes of the above measured concentration gradients results from the calculation of $(\partial x / \partial \Delta)_{TP}$ by eq. 3.18. Determining dX/dz from our values of A and δ by eq. 5.1 and estimating $(\partial v / \partial X)_{TP}$ by the methods outlined in Appendix D, we have calculated $(\partial \Delta / \partial X)_{TP}$ as a function of $(X - X_C)$ for the pressures we have employed. These relationships are plotted in Fig. 21 for values of $(X - X_C)$ for which we

Figure 21

A comparison with previous experimental work. Our calculated values of $(\partial\Delta/\partial X)_{TP}$ compared with those of Goellner and Meyer.¹³ The shaded area indicates the uncertainties in the data by Watts¹⁴ assuming $\delta = 2$.



we have data, along with the one resulting from our estimate of Watt's¹⁴ SVP concentration gradient. The data of Goellner and Meyer¹³ are displayed as well. As can be seen, our data appears entirely reasonable when compared to these previous results. This is especially true since Watts believes that systematic errors resulted in his underestimation of the concentration gradient near the TCP. It should be noted that our data covers another order of magnitude closer to the TCP.

The behavior of the concentration gradient and hence the concentration susceptibility under pressure deserves special attention. Although our density of points is low, the decrease in magnitude of $(\partial X/\partial \Delta)_{TP}$ between 2.5 and 9.9 atm. and its subsequent increase as the pressure is raised to 16.7 atm. strongly suggests that its behavior is analogous to the behavior, as a function of pressure, of both the $T=0K$ solubility of He^3 in He^4 and the value of X_C . More measurements at intermediate pressures will be necessary to confirm this. As mentioned in section 3D, we examined the Blume Emery and Griffiths model in hopes of shedding some light on this behavior. The pressure dependence thus predicted is exactly opposite to the one measured. The theoretical values of $(\partial \Delta/\partial X)_{TP}$ decrease as the pressure is increased from SVP to 9.9 atm. and then increase up to the solidification point. The concentration susceptibility assumes a reasonable value only for the $K \leq 0$ case. Furthermore, to achieve values of X_C close to the 9.9 atm value, both $\mathcal{K}$ and $(\partial \Delta/\partial x)_{TP}$ become negative.

A negative value of $(\partial\Delta/\partial X)_{TP}$ is indicative of physically unstable solutions.

B. The Pressure Dependence of the Tricritical Point

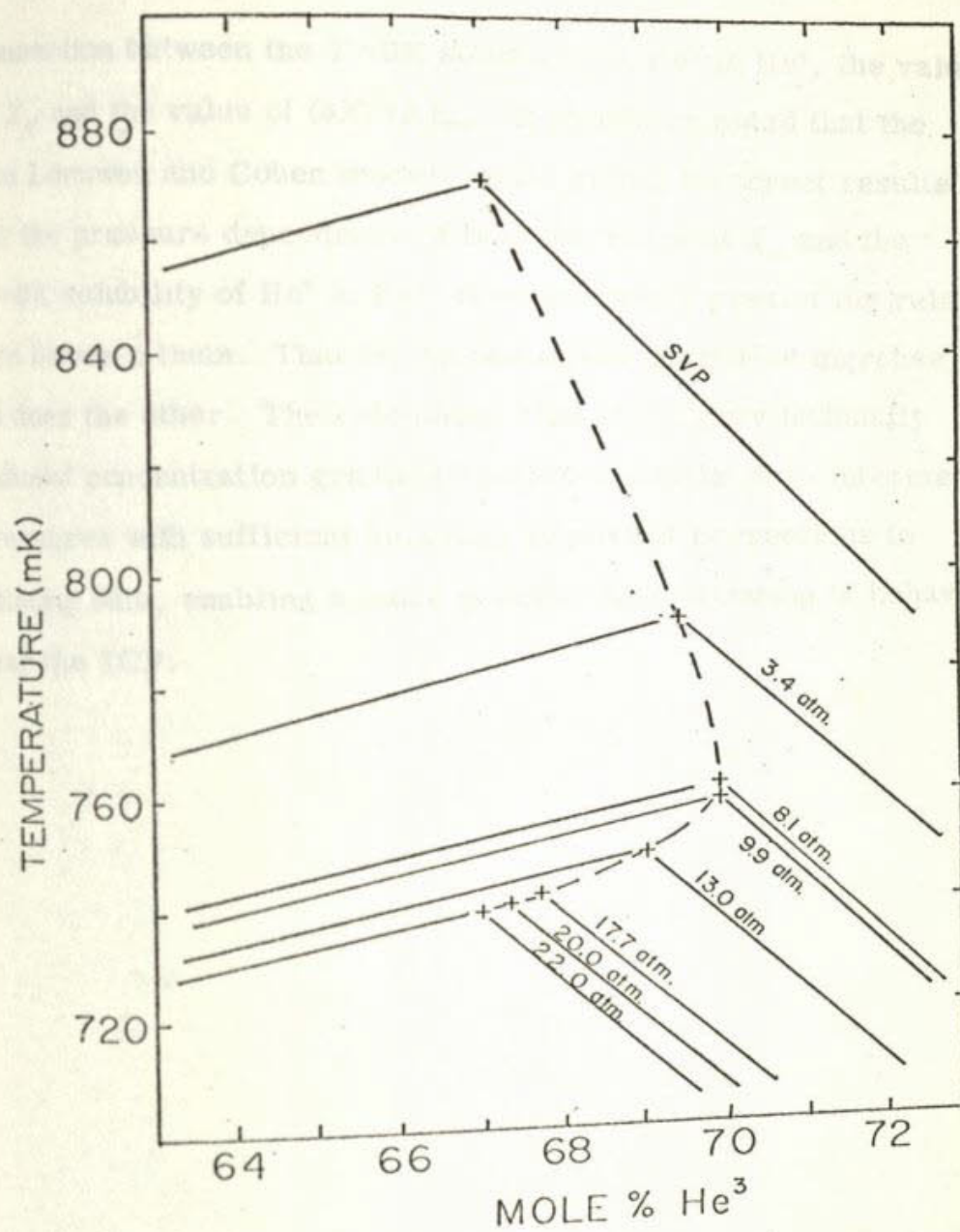
The magnitudes of the concentration gradients measured here, as well as the determination of that pressure for which X_c has a maximum value were used to correct the data of Johnson¹⁸ and Rohde¹⁹ near the TCP. The results of this correction are shown in Fig. 22, which demonstrates the motion of the TCP under pressure on an expanded scale. Where the gravitational gradient is large, corrections of .004 in concentration and 3 mK in temperature were common.

C. Conclusion

The exploration of the spatial distribution of concentration near the TCP is a powerful tool for the determination of both the magnitude and critical behavior of tricritical phenomena in He³-He⁴ mixtures. A careful determination of a large number of points at any pressure could determine the critical exponent to within a few percent. The spatial resolution also helps to give a much clearer picture of the dynamics of interfacial motion. The values of the critical exponent and the concentration susceptibility calculated from this data are in good agreement with theory and previous experiment. The variation of concentration susceptibility with pressure is both marked and remarkable suggesting a

Figure 22

The pressure dependence of the tricritical point. An enlargement of the significant portion of Fig. 2. Corrected data by Johnson¹⁸ and Rohde¹⁹.



connection between the $T=0\text{K}$ solubility of He^3 in He^4 , the value of X_c and the value of $(\partial X/\partial \Delta)_{\text{TP}}$. It should be noted that the van Leeuwen and Cohen model, while giving incorrect results for the pressure dependence of both the value of X_c and the $T=0\text{K}$ solubility of He^3 in He^4 , does correctly predict the relation between them. That is, as one of the quantities increase, so does the other. The calculated size of the gravitationally induced concentration gradient can be extrapolated to intermediate pressures with sufficient accuracy to permit corrections to existing data, enabling a more precise determination of behavior near the TCP.

Appendix A

If we choose $X=0.70$, an examination of the molar volume vs concentration curves*, Fig. 23, reveals that at SVP the molar volume is 33.4 cc and at 17.7 atm the molar volume is 27.0 cc. This, in turn, gives us a compressibility of 0.012 atm^{-1} .

In a sample chamber 10 cm high, the density of the mixture (.113 g/cc) leads to a pressure head of $1 \times 10^{-3} \text{ atm}$ at the bottom of the chamber. Thus, the variation in the density of the sample over this height is:

$$\frac{\Delta\rho}{\rho} = 1.2 \times 10^{-5} \quad (\text{A1})$$

Since the filling of the sample chamber corresponds to a frequency shift of $\sim 1.5 \times 10^5 \text{ Hz}$, the above variation in density corresponds to a change of less than 2 Hz over the entire height of the sample chamber. This is near the limit of resolution of the present apparatus.

*The origin of these curves is discussed in Appendix D

Appendix B

A number of Maxwell relations can be derived from the various thermodynamic potentials appropriate to this system. For example, choosing the molar Gibbs potential of eq. (3.7):

$$G = u - Ts + Pv$$

with:

$$dG = -s dT + v dP + \Delta dX$$

we can see that:

$$\left(\frac{\partial G}{\partial P}\right)_{TX} = v \quad \text{and} \quad \left(\frac{\partial G}{\partial X}\right)_{TP} = \Delta \quad (\text{B1})$$

So:

$$\frac{\partial^2 G}{\partial X \partial P} = \left(\frac{\partial v}{\partial X}\right)_{TP} \quad \text{and} \quad \left(\frac{\partial^2 G}{\partial P \partial X}\right) = \left(\frac{\partial \Delta}{\partial P}\right)_{TX} \quad (\text{B2})$$

but, the above second partial derivatives must be equal, giving:

$$\left(\frac{\partial v}{\partial X}\right)_{TP} = \left(\frac{\partial \Delta}{\partial P}\right)_{TX} \quad (\text{B3})$$

By choosing other potentials and other derivatives a whole series of these relations can be built up:

$$\left(\frac{\partial P}{\partial X}\right)_{vT} = -\left(\frac{\partial \Delta}{\partial v}\right)_{PT} \quad (\text{B4})$$

$$\left(\frac{\partial v}{\partial X}\right)_{TP} = \left(\frac{\partial \Delta}{\partial P}\right)_{TX} \quad (\text{B5})$$

$$\left(\frac{\partial v}{\partial \Delta}\right)_{TP} = -\left(\frac{\partial X}{\partial P}\right)_{T\Delta} \quad (B6)$$

$$\left(\frac{\partial \Delta}{\partial P}\right)_{SX} = \left(\frac{\partial v}{\partial X}\right)_{SP} \quad (B7)$$

$$\left(\frac{\partial P}{\partial \Delta}\right)_{Sv} = \left(\frac{\partial X}{\partial v}\right)_{S\Delta} \quad (B8)$$

$$\left(\frac{\partial P}{\partial \Delta}\right)_{Tv} = \left(\frac{\partial X}{\partial v}\right)_{T\Delta} \quad (B9)$$

$$\left(\frac{\partial \Delta}{\partial P}\right)_{SX} = \left(\frac{\partial v}{\partial X}\right)_{SP} \quad (B10)$$

In this work, only relation B3 is employed.

Appendix C

This is a derivation of the critical behavior predicted by the Blume, Emery and Griffiths²⁶ model, solved in the mean field approximation, for general $\mathcal{J}$ and $\mathcal{K}$ parameters. For the superfluid case, ($M \neq 0$), it is possible to divide eq. (3.55) by eq. (3.56) to obtain

$$1 - X = M \coth \beta \mathcal{J} M \quad (C1)$$

Expanding the hyperbolic cotangent and setting $\mathcal{J} = 1$:

$$1 - X = M \left(\frac{1}{\beta M} + \frac{1}{3} \beta M - \frac{(\beta M)^3}{45} + \frac{2(\beta M)^5}{945} \dots \right) \quad (C2)$$

In order to go over the reduced variable $x = X_c - X$, we note that Blume, Emery and Griffiths have calculated:

$$X_c = \frac{2}{2\mathcal{K} + 3} ; \beta_c = \frac{1}{1 - X_c} = \frac{2\mathcal{K} + 3}{2\mathcal{K} + 1} \quad (C3)$$

So

$$x = \frac{\beta}{3} M^2 - \frac{\beta^3 M^4}{45} + \frac{2\beta^5 M^6}{945} \dots \quad (C4)$$

This series can be inverted to give:

$$\beta^2 M^2 \cong 3\beta x + \frac{\beta^4 x^2}{15} + O(x^3) \quad (C5)$$

We can re-write eq. (3.55) as:

$$\exp\{\beta[\Delta - \mathcal{K}(1-X)]\} = \frac{2X}{1-X} \cosh\beta M \quad (\text{C6})$$

If we divide this equation by an identical one in which Δ and X have taken on their critical values, ($M=0$), and take the reciprocal, we arrive at:

$$\exp\{\beta(\Delta_c - \Delta)\} = \exp\{\beta\mathcal{K}(X - X_c)\} \frac{2(1-X)}{(2\mathcal{K}+1)X \cosh\beta M} \quad (\text{C7})$$

or:

$$\begin{aligned} \beta(\Delta_c - \Delta) = & -\beta\mathcal{K}(X_c - X) + \ln\left(\frac{2}{2\mathcal{K}+1}\right) + \ln(1-X) - \ln(X) \\ & - \ln[\cosh\beta M] . \end{aligned} \quad (\text{C8})$$

Substituting $(X_c - x)$ for X in the above equation and expanding the last three terms leads to:

$$\begin{aligned} \beta(\Delta_c - \Delta) \cong & -\beta\mathcal{K}x + \ln\left(\frac{2}{2\mathcal{K}+1}\right) + \frac{x}{1-X_c} - \frac{x^2}{2(1-X_c)^2} + \dots \\ & + \ln(1-X_c) - \ln(X_c) + \frac{x}{X_c} + \frac{x^2}{2X_c^2} + \dots \\ & - \frac{(\beta M)^2}{2} + \frac{(\beta M)^4}{12} + \dots \end{aligned} \quad (\text{C9})$$

Substituting our value for $\beta^2 M^2$ from eq. (C5) into (C9) and gathering together like terms, leads, after much cancellation, to:

$$\Delta_c - \Delta = x^2 \left[\frac{480\mathcal{K}^5 + 1680\mathcal{K}^4 + 2368\mathcal{K}^3 + 1776\mathcal{K}^2 + 594\mathcal{K} + 27}{120(2\mathcal{K}+1)^3} \right] \quad (\text{C10})$$

Thus, $\delta=2$ and the amplitude of $(\partial\Delta/\partial x)_{TP}$ and hence the concentration gradient is a strong function of $\mathcal{K}$.

For the normal fluid case, ($M=0$), we can simply look at eq. (3.55) with $M=0$. This gives:

$$\exp\{\beta\Delta\} = \exp\left\{\beta\mathcal{K}(1-X) \frac{2X}{1-X}\right\} \quad (C11)$$

Proceeding analogously to the derivation above, we arrive at

$$\exp\{\beta(\Delta_c - \Delta)\} = \frac{4}{2\mathcal{K}+1} \frac{(1-X)}{2X} \exp\{\beta\mathcal{K}(X - X_c)\} \quad (C12)$$

Taking the logarithms of both sides of this equation and, as before, substituting $(X_c - x)$ for X we get:

$$\begin{aligned} \beta(\Delta_c - \Delta) = & \ln\left(\frac{2}{2\mathcal{K}+1}\right) + \ln\left(\frac{1-X_c}{X_c}\right) - \frac{x}{1-X_c} - \frac{x^2}{2(1-X_c)^2} \\ & - \frac{x}{X_c} + \frac{x^2}{2X_c^2} + \beta\mathcal{K}X \end{aligned} \quad (C13)$$

which, after some cancellation, leads to:

$$\Delta_c - \Delta = -\frac{3}{2}x + \frac{(2\mathcal{K}-1)(2\mathcal{K}+3)^2}{8(2\mathcal{K}+1)} x^2 + \dots \quad (C14)$$

Thus, in the normal phase $\delta=1$ and the magnitude of the concentration gradient is independent of $\mathcal{K}$ to first order.

Appendix D

The concentration sensitivity of the TDO can be derived as follows: the oscillator frequency is a measure of the dielectric constant, ϵ , of the material in between the plates of the tank circuit capacitor. This frequency is given by:

$$f = \frac{1}{2\pi\sqrt{L(\epsilon C + C')}} \quad (D1)$$

Where L is the total inductance of the tank circuit, C is that part of the total capacitance which "sees" the sample and C' is the remaining "stray" capacitance. A rearrangement of terms gives:

$$\epsilon = \frac{1}{4\pi^2 L C f^2} - \left(\frac{C'}{C}\right) \quad (D2)$$

Our first task is to determine the magnitude of C' . From (D1) it can be seen that if the sample chamber is empty, the frequency, f_0 , will be given by:

$$f_0 = \frac{1}{2\pi\sqrt{LBC}} \quad \text{where } B = 1 + \frac{C'}{C} \quad (D3)$$

Substituting (D3) into (D2) results in

$$\epsilon - 1 = B \left(\frac{f_0^2}{f^2} - 1 \right) \quad (D4)$$

In order to evaluate B the sample chamber was first evacuated and then filled with He^4 . The frequencies before and after filling

were noted. The dielectric constant of pure He^4 at SVP is known from data by Kerr and Sherman³⁷ and thus B may be calculated. The results of this procedure were:

$$f_0 = 11,544,096 \pm 5$$

$$f = 11,395,760 \pm 5$$

$$\epsilon = 1.0573 \pm .00005$$

$$B = 2.19 \pm .01$$

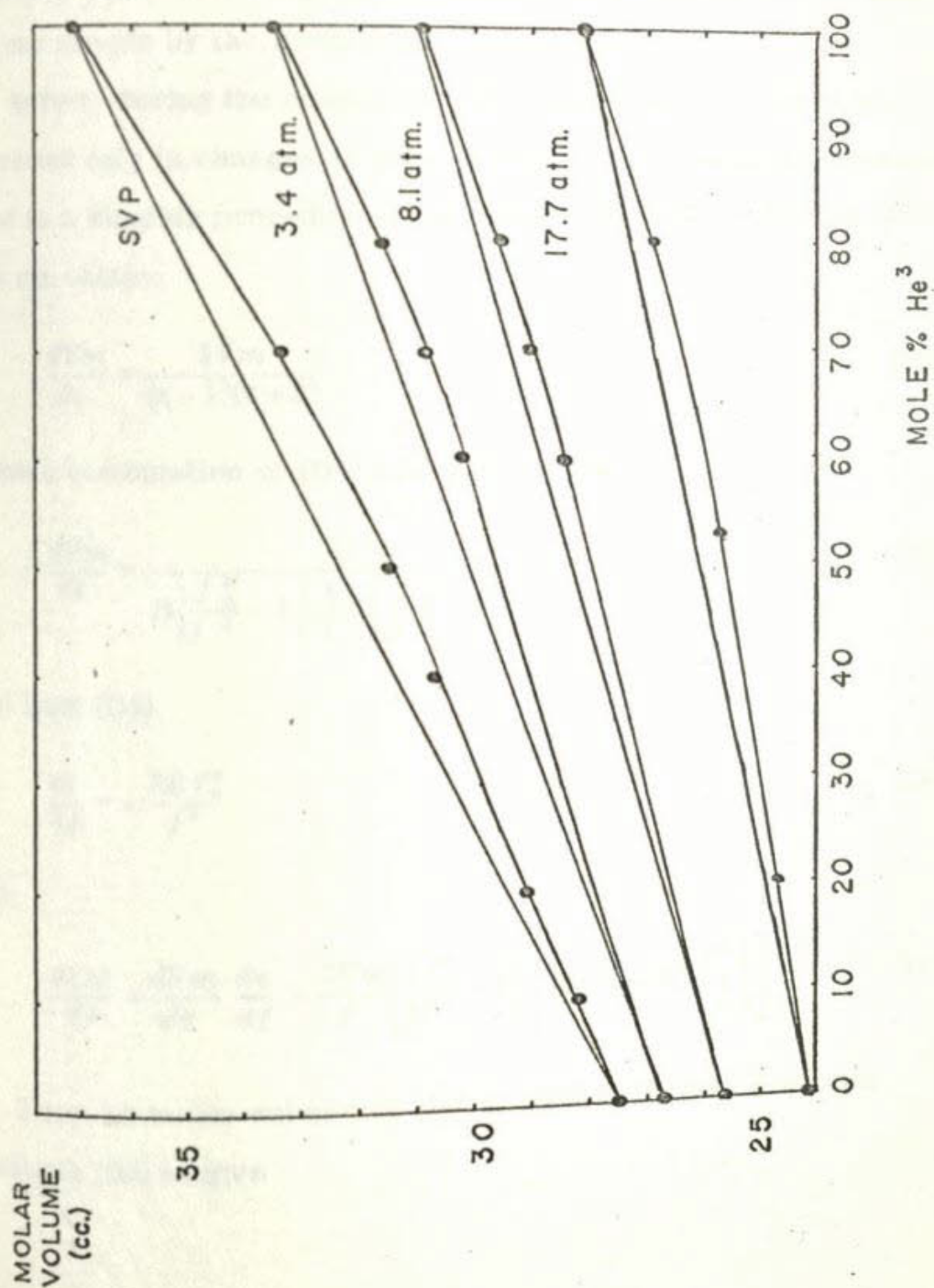
Once B is known, changes in frequency can be equated with changes in dielectric constant. The dielectric constant can be related to the molar volume of the sample by the Clausius-Mosotti relation:

$$V_m = \frac{4\pi P}{3} \frac{\epsilon + 2}{\epsilon - 1} \quad (\text{D5})$$

where P is the molar polarizability of helium, which is, for our purposes, the same for He^3 and He^4 ,³⁷ and V_m is the molar volume of the sample. Finally, the molar volume of the sample can be related to its concentration by generating a set of V_m vs. X curves at various pressures. Such a set of curves is shown in Fig. 23. The data for pure He^4 is by Kerr and Sherman³⁷ and Keesom³⁸ and the data for pure He^3 is by Sherman and Edeskuty³⁹. Data at intermediate points at SVP is due to Kerr⁴⁰. The curves at higher pressures were arrived at from analysis of the data of

Figure 23

Molar volume vs. concentration curves for He^3 - He^4 mixtures. Straight lines indicate ideal solution behavior. SVP data is due to Kerr.⁴⁰ The data for $X=0$ is by Kerr and Sherman³⁷ and Keesom³⁸. The data for $X=1$ is by Sherman and Edeskuty³⁹. Intermediate points at elevated pressure were arrived at by analysis of the data of Johnson¹⁸ and Rohde¹⁹.



Johnson¹⁸ and Rohde¹⁹, who measured the molar volumes at two intermediate concentrations exactly, and extrapolated the remainder of the curves on the basis of self-consistency arguments. We can, thus, in principle, determine the absolute concentration of our sample by the method outlined above.

In fact, during the course of this experiment, we were interested only in changes in concentration relative to the average, and so a simpler procedure is possible. By differentiating (D5) we can obtain:

$$\frac{dVm}{d\epsilon} = \frac{3Vm}{(\epsilon - 1)(\epsilon + 2)} \quad (D6)$$

Then a combination of (D4) and (D6) yields:

$$\frac{dVm}{d\epsilon} = \frac{3Vm}{B \left\{ \frac{f_0^2}{f^2} - 1 \right\} \left\{ B \left(\frac{f_0^2}{f^2} - 1 \right) + 3 \right\}} \quad (D7)$$

but from (D4)

$$\frac{d\epsilon}{df} = - \frac{2Bf_0^2}{f^3} \quad (D8)$$

So:

$$\frac{dVm}{df} = \frac{dVm}{d\epsilon} \frac{d\epsilon}{df} = \frac{6Vm}{f} \left[\left\{ \frac{f_0^2}{f^2} - 1 \right\} \left\{ B + (3 - B) \frac{f^2}{f_0^2} \right\} \right]^{-1} \quad (D9)$$

Since the molar volume of He⁴ at SVP is 27.52 cc we can evaluate (D9) to give

$$\frac{dVm}{df} = 1.83 \times 10^{-4} \quad \text{at that pressure .} \quad (\text{D10})$$

Then the concentration sensitivity of the oscillator may be found thusly:

$$\frac{dX}{df} = \frac{dX}{dVm} \frac{dVm}{df} \quad (\text{D11})$$

Since over the course of a run the changes in X and f are very small compared to their values — no more than 1% — we can assume that:

$$\Delta X = \frac{dX}{dVm} \frac{dVm}{df} \Delta f \quad (\text{D12})$$

Values of dX/dVm can be estimated at any pressure from the values of Vm for pure He^3 and pure He^4 at that pressure. As can be seen from the curves of Fig. 23 the approximation that:

$$\frac{dX}{dVm} = \frac{1.0 - 0.0}{Vm(\text{He}^3) - Vm(\text{He}^4)}$$

is quite good in the range of interest $-0.67 \leq X \leq 0.70$ as the tangent and chord of the curves are nearly parallel in that range.

Bibliography

1. F. C. Nix and W. Shockley, Rev. Mod. Physics 10 (1938) 1
2. I. S. Jacobs and P. E. Lawrence, Phys. Rev. 164 (1967) 866
3. D. P. Landau, B. E. Keen, B. Schneider and W. P. Wolf, Phys. Rev. B3 (1971) 2310
4. W. J. Moore, *Physical Chemistry*, (Prentice-Hall Inc., 1972) 257
5. R. L. Johnson, Ph. D. Thesis, SUNY at Stony Brook (1973)
6. P. Leiderer, D. R. Watts and W. W. Webb, Phys. Rev. Lett. 33 (1974) 483
7. B. M. Abraham, B. Weinstock, and D. W. Osborne, Phys. Rev. 76 (1949) 864
8. G. K. Walters and W. M. Fairbank, Phys. Rev. 103 (1956) 262
9. E. H. Graf, D. M. Lee and J. D. Reppy, Phys. Rev. Lett. 19 (1967) 417
10. K. W. Taconis and R. DeBruyn Ouboter, *Prog. Low Temp. Physics*, ed. C. J. Gorter (North Holland Publishing Co., Amsterdam, 1964) V. 4 p. 38
11. V. N. Peshkov, Sov. Phys. Uspekhi 11 (1968) 209
12. T. Alvesalo, P. Berglund, S. Islander and W. Zimmermann Phys. Rev. Lett. 22 (1969) 1281; Phys. Rev. A4 (1971) 2354; S. T. Islander and W. Zimmermann, Phys. Rev. A7 (1973) 188
13. G. Goellner and H. Meyer, Phys. Rev. Lett. 26 (1971) 1534
14. D. R. Watts, Ph. D. Thesis, Materials Science Center, Cornell University (1973)
15. G. Ahlers and D. S. Greywall, Phys. Rev. Lett. 29 (1972) 849
16. G. Ahlers and D. S. Greywall, *Proc. of the 13th International Conf. on Low Temp. Physics* (Boulder, CO., 1972)

17. C-M Lai, Ph. D. Thesis, SUNY at Stony Brook (1973)
18. R. L. Johnson, Ph. D. Thesis, SUNY at Stony Brook (1973)
19. T. Rohde, unpublished work, SUNY at Stony Brook (1975)
20. G. E. Watson, J. D. Reppy and R. C. Richardson, Phys. Rev. 188 (1969) 384
21. R. B. Griffiths, private communication
22. E. G. D. Cohen and M. J. M. van Leeuwen, Phys. Rev. 176 (1968) 385
23. J. M. Kincaid and E. G. D. Cohen, Physics Reports 22 #2 (1975), 57
24. T. D. Lee, K. Huang and C. N. Yang, Phys. Rev. 106 (1957) 1135; T. D. Lee and C. N. Yang, Phys. Rev. 112 (1958) 1419
25. J. M. Kincaid, Ph. D. Thesis, The Rockefeller University (1974)
26. M. Blume, V. J. Emery and R. B. Griffiths, Phys. Rev. A4 (1971) 1071
27. D. M. Saul and M. Wortis, *A.I.P. Conference Proceedings Vol V* (USA, 1971) 349; Phys. Rev. B9 (1974) 4964
28. S. Takagi, Prog. Theor. Physics, 47 (1972) 22
29. T. Matsubara and H. Matsuda, Prog. Theor. Physics, 16 (1956) 569
30. R. P. Siemann and D. L. Huber, Phys. Rev. B15 (1977) 2581
31. E. K. Riedel and F. J. Wegner, Phys. Rev. Lett. 29 (1972) 349
32. K. G. Wilson, Phys. Rev. B4 (1971) 3174
33. L. P. Kadanoff *et al.*, Rev. Mod. Physics 39 (1967) 395
34. O. W. G. Heybey, Thesis, Cornell University (1962)

35. T. R. Roberts, R. H. Sherman, S. G. Sydoriak and F. R. Brickwedde, *Prog. Low Temp. Physics*, ed. C. J. Gorter (North Holland Publishing Co., Amsterdam 1964) vol. 4 p. 480
36. P. R. Roach, *Phys. Rev.* 170 (1968) 213
37. E. C. Kerr and R. H. Sherman, *Journal of Low Temp. Physics* 3 (1970) 451
38. W. H. Keeson, *Helium* (Elsevier, 1942) 240
39. R. H. Sherman and F. T. Edeskuty, *Annals of Physics* 9 (1960) 522
40. E. C. Kerr, *Proc. of the 5th International Conf. on Low Temp. Physics* (University of Wisconsin, 1957) 180
41. J. G. Daunt and C. V. Heer, *Phys. Rev.* 79 (1950) 46
42. J. G. Dash and R. D. Taylor, *Phys. Rev.* 99 (1955) 598
43. V. P. Peshkov and K. N. Zinov'eva, *Sov. Physics JETP* 37 (1960) 22
44. T. R. Roberts and S. G. Sydoriak, *Physics of Fluids* 3 (1960) 895
45. De Bruyn Ouboter, Taconis, Le Pair and Beenakker, *Physica* 26 (1960) 853